

CLEAN FUELS FROM COAL: THE PATH TO 1972.

Burtron H. Davis

Center for Applied Energy Research, University of Kentucky
2540 Research Park Drive, Lexington, KY 40511

During its infancy, the United States utilized renewables as its source of energy. With time, coal became the dominant source of energy for home, industry and transportation and gradually replaced renewables during the 1800s. During this period the conversion of coal to gas was developed and grew in use until natural gas subsequently supplanted it. Scientific advances in the utilization of coal began with the establishment of the US Bureau of Mines and the German laboratory in Mulheim, among others, in the early 1900s. The period 1920-40 has been characterized as the flowering era of fuel science and technology. A brief perturbation was superimposed on the research activities for coal by the fear of an oil shortage during 1944-1953 but this emphasis declined with the exploitation of Mid-East oil. The oil crisis of 1972 set the stage for the activities for the period of the current symposium: 1972-2002.

Introduction

Humans, as gatherers, utilized renewable resources. With the use of domestic animals for transportation and agriculture, the utilization of energy by humans increased, but still depended on renewable resources. Growth of human population caused an escalation of energy usage to the point where forests nearly vanished in "developed" countries in the 1600s. In Great Britain, the shortage of forests was overcome by substituting a stored fossil fuel, coal. The high density of energy stored in coal gradually caused developing countries with coal reserves to switch to it for their energy sources. Even so, transportation and agriculture was still accomplished by energy derived from humans and domesticated animals.

With the introduction of the steam engine, the situation changed dramatically. Rather than an evolutionary escalation of the use of energy, there was an abrupt, revolutionary increase in the use of energy. Based on this increased use of energy, the productivity of each human and their ability to travel great distances could also undergo a revolutionary advance, and this happened. As shown in Figure 1, evolutionary and revolutionary advances in mechanical developments and theoretical understanding now permit the efficiency of a steam engine to approach its ultimate value

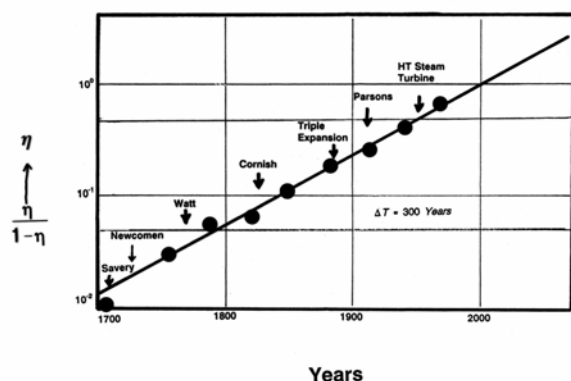


Figure 1. Evolution of steam engine efficiency η (Fisher-Pry notation).

The primary energy in the U.S. in 1800 was wood, a renewable resource. However, as energy use increased coal gradually displaced wood (Figure 2). Coal was at a later time replaced by oil and natural gas. Nuclear was destined to become a dominant source of energy for the U.S., but political controversy led to its loss of favor and no new plants have gone on-stream during the past 20 years.

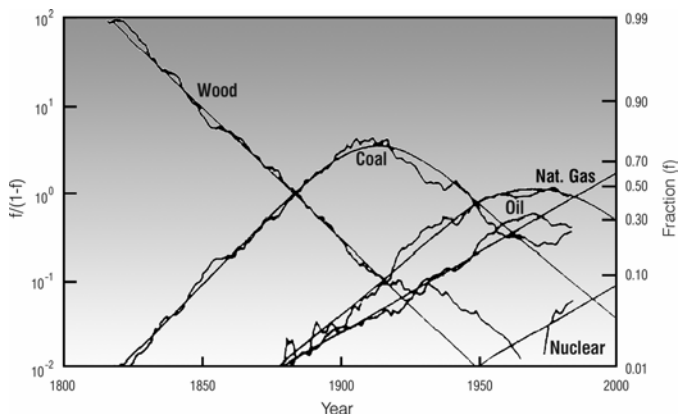


Figure 2. The distribution of fuel usage during 1800 to 2000.

Figure 3 shows the distribution by mileage of intercity transportation in the U.S. Early travel was predominantly by canals and this was replaced, first by rail and then by auto/truck traffic. More recently air travel has shown growth and, because of the long distances for plane travel, will soon replace the auto for intercity transportation. Fuel usage by transportation had a significant influence on the form of energy used. Rail transportation was the dominant mode until well into the 20th century. Coal gradually replaced wood as the fuel of choice and maintained this dominance through the WW II period and was then rapidly replaced by diesel powered electric trains. The use of coal in transportation was accomplished with inefficient combustion and the emission of large quantities of ash and soot. Black skies and buildings in major cities resulted from this incomplete combustion without control measures and this was tolerated, or even encouraged, as the cost of the industrial revolution.

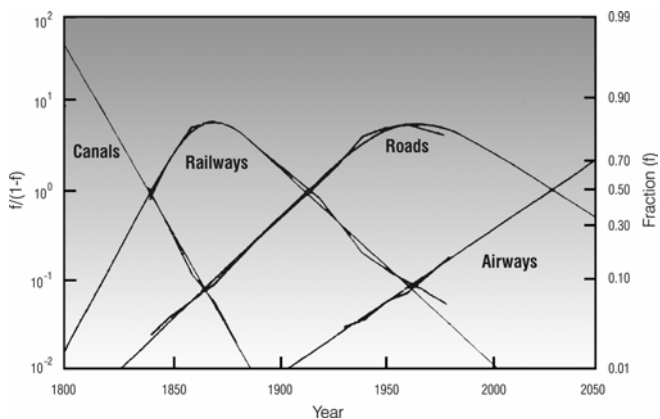


Figure 3. Distribution of mode of inner-city travel.

Coal-based industries developed that were based on the by-product tars from the coke ovens. Coke ovens lining highways and rivers leading into Pittsburgh, for example, emitted sufficient light and smoke that night sky glowed and was described by an observer as

“Hell with the roof off.” By 1950 the glow started to dim and petroleum began to become the dominant feedstock for the chemical industry.

During the 1800s the general theme of the U.S. was expansion. As natural resources were reduced so that they could no longer meet demand, the population either concentrated in cities in the eastern U.S. or moved West. For example, the population of New York City was about 30,000 people in 1800 but had grown to about 4.5 million by 1900. Coal replaced wood and, as it was used at that time, it was a dirty fuel. But so was the renewable that it displaced: wood. Likewise, transportation depended upon horses, and these also were dirty. New York City had about 200,000 horses in 1900 and each horse produced about 24 pounds of manure and several quarts of urine. During the winter, the accumulation of snow and horse wastes could reach 2 to 6 feet in the streets of NYC. The conditions that the horses were exposed to resulted in a life expectancy of less than three years. The “dirty coal” images lives on but the even dirtier alternatives have been forgotten. The advantages of coal greatly outweighed the disadvantages, judged by the conditions of that time. Thus, the growth of coal usage was rapid up to about 1925.

As research on coal intensified at the beginning of the 20th century, processes were soon developed that could convert the solid into liquid transportation fuels. The Bergius Process for the direct liquefaction of coal using high reaction temperatures and high hydrogen pressures was announced in the 1910s. In the following decade, the process now known as the Fischer-Tropsch synthesis was announced, and coal could be converted first to a synthesis gas and then to liquid hydrocarbons. Today it is easy to overlook the significance of these discoveries. The following extract gives one a flavor of the magnitude of these advances placed in the time of the discoveries (H. Elkwood, J. Chem. Educ., 2, 631 (1925)).

One of the unsolved riddles of chemistry is the precise constitution of a lump of coal. There are combinations of carbon and hydrogen and oxygen and nitrogen there that go to pieces as soon as we undertake to find out just what they are. Now a German chemist named Bergius has succeeded, principally by means of high pressures, in introducing hydrogen into heavy oils and also into bituminous coal so that the latter takes on the liquid character of a crude petroleum. Suppose, then, that some chemist were to discover a catalytic method of hydrogenating bituminous coal so that it becomes liquid and that this method should become economically possible. **Please close the book for a few moments at this point and think what such a discovery would mean. Liquid fuel for everything. No more stoking, no more smoke or cinders, no more worry about the waning supply of petroleum and no more coal bins (emphasis added).**

Since 1925 when Elkwood wrote the above, we have come close several times to attaining his dream only to find an additional source of petroleum, and coal usage continued to decline.

The increasing use of coal and other fossil fuels together with the results from the scientific centers established around the world led to results that could make the period of 1925-1940 the flowering era of fuel science and technology [M. A. Elloit, Preprints, ACS Division of Fuel Chemistry 19(3), 140-161 (1974).] In the field of combustion this period saw the extensive development of the burning of pulverized coal under slagging conditions to generate steam and a greatly improved understanding of the kinetics and mechanism of the combustion of solid fuels. Coal gasification technology was advanced: by the development of gasifiers using oxygen; by operating at elevated pressures, under slagging conditions, and with a

fluidized bed; and by demonstrating the feasibility of hydrogasification. During the period the efficient by-product coke oven almost completely replaced the beehive oven for producing metallurgical coke. Coal liquefaction and solvation progressed from the laboratory to the full-scale commercial plant. The Fischer-Tropsch process was discovered and progressed to the commercial stage during this period. Major advances were made in knowledge of the kinetics and mechanism of the oxidation of gaseous fuels and in knowledge of the properties of fuel-air mixtures. Extensive work was done on the chemical constitution of coal and tar and on their physical properties. These advances are detailed in Elliott's paper.

During 1940-1960, war played a dominant role in the use of fuel during the early years of this period. Based on tonnage, petroleum products were the major export from the U.S. to European Allies. Even so, the Allies were required to make dramatic adjustments in lifestyle. Shown in Figure 4 is an auto on a street in Paris, modified to run on gases generated by the “on-board garbage-can gasifiers” mounted on the front of the auto.



Figure 4. On-board gasifier for auto transportation during WWII in Paris, France.

During this period it was recognized that the U.S. was facing a future supply problem for transportation fuels. The Synthetic Liquid Fuels Act went into effect in 1944 and the research at the Bureau of Mines, started in 1936, underwent a large and rapid expansion. Bench- and pilot-scale plants were operated at the labs in Pittsburgh with emphasis on new catalysts, effects of process variables and reaction mechanisms. These studies were incorporated together with results from

German operations in the demonstration plant that was built in Louisiana, Missouri. The direct coal liquefaction demo plant processed about two tons coal per hour to produce about 200 bbl/day of products. Emphasis was on operability and much progress was made. Fischer-Tropsch synthesis received much support. The high-temperature fluid bed operation to produce mainly gasoline was favored by petroleum companies. A commercial scale plant using a fixed-fluid catalyst bed reactor was built near Brownsville, Texas. Just as operational problems were overcome, the discovery of large quantities of Mid-East oil at low prices caused the plant to be closed. In South Africa, the need for energy independence led the government to support the Sasol plant that utilized circulating fluid-bed reactors. The other approach involved several modifications of low-temperature operations utilizing fixed-bed catalytic reactors, bubble column reactors and variations between these two extremes of operation. A demonstration plant was constructed and operated at the Louisiana, Missouri plant. In Germany, a demonstration plant using

the bubble column reactor was operated. However, these plants were also victims of the increased supply of cheap oil.

During the 1940-60 period, coal gasification was a major topic. A variety of processes advanced up to bench scale units (100-500 pounds of coal per hour). Most of these were designed to operate at pressures that would permit purification and Fischer-Tropsch operation without additional compression. Nearly all of these processes utilized oxygen. However, during this period, only two plants were built at a larger scale. The Bureau of Mines operated at Louisiana, Missouri a Linde-Frankie oxygen plant that produced 25 tons per day and this was fed to a suitably sized Koppers-Totsaek coal gasifier. Du Pont built a plant at Belle, West Virginia to produce 25 million cubic feet of hydrogen per day and this was operated successfully for two years using coal. However, after two years, operations were terminated and natural gas became the source of the hydrogen.

As it was recognized that U.S. demand for liquid hydrocarbons could be met using foreign oil to augment internal production, the Office of Synthetic Liquid Fuels was eliminated in 1953. The demonstration plants were closed, laboratory staff was reduced and the research emphasis was shifted to other topics.

The 1960-1980 period provides two extremes. During the late 1950s and early 1960s gasoline was plentiful and low priced; service station operators, backed by petroleum companies, offered many incentives for customers to buy more of their products. The muscle cars of that era consumed large quantities of gasoline, much as SUVs do today. U.S. petroleum production was subsidized by two means during this period. Petroleum producers were allowed significant tax advantages in the form of allowances for their depletion of U.S. reserves. In addition, refiners were to limit imports to no more than 25% of their production. Thus, U.S. production was artificially priced at about \$4.50/bbl when mid-East crude would be obtained for \$2.25/bbl at U.S. coast ports. Thus, U.S. government actions were accelerating the depletion of U.S. crude reserves while indirectly subsidizing the oil industry in its competition with coal. The picture dramatically changed as the 1970s two oil price shocks with very high prices and shortage of supplies. The U.S. and other developed countries started crash programs to convert coal to liquid fuels. Pilot plants for direct coal liquefaction were constructed in the U.S. that processed up to 600 tons of coal per day. During this period, one state (Kentucky) had 12 commercial coal-based plants at some stage of design as well as others based on oil shale and tar sands. During the 1970s the public expected the worst and projections supported this fear (Figure 5). The oil shocks also

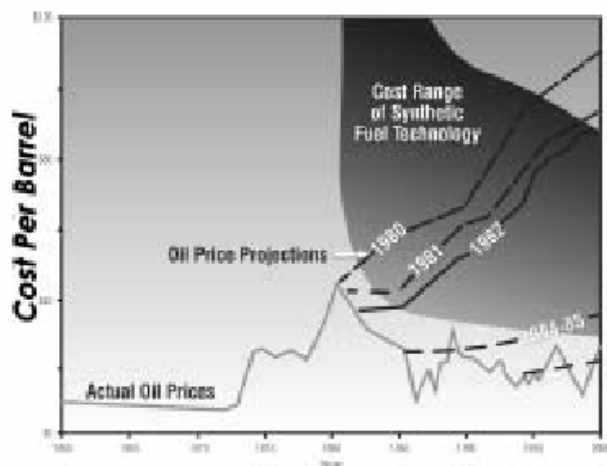


Figure 5. Projected and actual prices for crude.

changed perceptions in other ways. The straight line portion of Figure 6, covering the period 1950-1974 showed a straight line relationship between energy consumption and the U.S. gross national product (GNP). The linear relationship was shown to be one of convenience since the increase in oil prices caused dramatic and rapid changes, determined primarily by conservation and by exporting energy intensive industries to other countries.

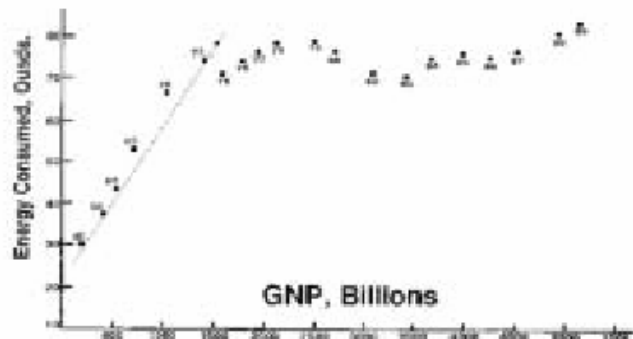


Figure 6. Relation of energy consumption and GNP for U.S. (Numbers in figure are for year; eg., 65 is 1965).

History shows that it has been very difficult to predict the future of coal and of the development of a synfuels industry. Predicting the progress of clean fuels from coal is especially fitted by the quote attributed to Niels Bohr: "It is very difficult to make predictions, especially when it is about the future!!". Clean fuels from coal is here today for the generation of electrical power, and it gets cleaner each year. Coal can provide clean fuels for transportation and this will become necessary for the U.S., the difficulty is to predict when this will occur.

References

1. B.H. Davis, *Energieia*.
2. H. Elkwood, *J. Chem. Educ.*, 2, 631 (1925).
3. M.A. Elloit, *Preprints, ACS Division of Fuel Chemistry* 19(3), 140-161 (1974).

Progress of Coal Science in the 20th Century

Karl H. van Heek

Fährenkotten 3, D - 45259 Essen, Germany

Abstract

The Lecture deals with the development and advances of coal science in the last century under the driving forces of politics, economics, and technology and in interaction with the progress achieved by other scientific and engineering disciplines. The growth and status of knowledge is demonstrated choosing examples under the guideline "Structure and Basic Reactions". The contribution is based on the author's publication in *Fuel* 79 (2000) 1-26.

Keywords: coal science, history, methods, structure, reactions, progress

Coal Science in the Political and Technological Context of the Century

No doubt, the reader will be aware of the fact, that coal has been the dominant source of energy, for coke and for chemicals, throughout the world for long periods in the past two centuries of industrialisation and still is at present and will be in the future in many countries. Thus the readiness of the best technology for its conversion and use has been and still is a prominent factor for the development of the international economy and consequently the subject of strategic considerations and measures.

At the beginning of the century the enormously increasing demand for energy, for industrial use, transportation and homes in interplay with the nations' efforts for self-sufficiency spurred the industrialised countries to intensify research into improved utilisation of their fossil fuels. The First World War and the post wartime made the strategic and economic rank of coal even more evident, stressing the necessity of intensified relevant research also. New scientific journals appeared e. g.: "*Brennstoff-Chemie*" (Fuel-Chemistry) in Germany and "*Fuel*" in Great Britain both in 1921/22. Economic strategies and political interests and the attraction of coal for science along with methods and instruments under development in physics and chemistry pushed progress of coal technology and research at that period. Their outcome in petrology, characterisation and classification of coal, in developing direct and indirect liquefaction and the first steps to explain mechanisms and kinetics of reactions are admirable. Some outstanding examples must be mentioned:

In 1913 at an age of 27 years *Friedrich Bergius* made studies into the application of high pressure and temperature. In doing so, a pure academic work for clearing up coalification became the immediate fundament of direct liquefaction of coal¹. In 1921 *Fritz Winkler*, 33 years old, investigated the possibility to produce activated carbons by partial gasification of lignite with steam. Thereby he detected the phenomena of fluidisation in the "Winkler Reactor"² named after him. The synthesis of liquid hydrocarbons was discovered by *Franz Fischer* and *Hans Tropsch* in 1926, as a fruit of coal orientated activities³. Pioneering work was carried out during the 30ies in the field of kinetics of carbon combustion at the MIT under the direction of *Hoyt C. Hottel*^{4,5}. They discovered the principles of macrokinetics of gas-solid reactions occurring in coal combustion, which in the meantime became a well-known theory for gas-solid reactions in porous solids.

The enthusiasm and results of coal research going on from that characterises the situation in the 50s and early 60s also. During this phase a whole series of public or private institutions had been founded, stimulating coal research. A series of in total 7 international

biennial conferences with up to say 160 participants started in 1955, a sign of the increased self-confidence of coal scientists. In the late 50s however, oil, natural gas and even nuclear energy had grown up into challenging competitors pushing coal from the first place: Coal and its science lost interest in a dramatically short period of time.

However this wine of seeming abundance of energy and fuel was watered down relatively soon by the message of the "Club of Rome": Supplies of fossil fuels and other resources are limited, especially those of oil and natural gas. Leaders in politics, industry and science reflected on coal again: In the USA it was the program "Substitute Natural Gas (SNG) from Coal" starting in the 60s. New perspectives had been opened for coal science and technology⁶. A large variety of processes and concepts on *hydrogasification* were proposed for development and research⁷. The German development of a nuclear-aided gasification processes was initiated in 1968^{8,9}. The impact of this approach on coal science especially on the investigation of gasification of coal and lignite¹⁰ in Germany at the end of the 60's was enormous.

From October 1973 onwards the banner of coal science seemed to be erected again for good. A sudden shortage of oil along with a dramatic rise in price, unexpectedly for many of us, stimulated energy research in practically all areas. A fresh impetus was given to research into the chemical and physical structure of coal, as well as its gasification and hydrogenation, as the basis of development of new, and optimisation of known, technical processes¹¹. Coal science was going strong and as evidence of it the ICCS was revived in 1981 by initiative of the "International Energy Agency-IEA" and its "Working Party on Coal". Financially supported by the public and by private industries of Australia, Germany, Japan, Canada, The Netherlands, Spain, UK, USA and at the beginning also of Sweden, the Conferences took place biennially, hosting often more than 500 participants^{12,13,14,15,16,17,18,19,20}. The last one took place in China⁹⁹.

- After years of concentration among the publications on coal science publication, new journals appeared. "Fuel Processing Technology" started in 1977, and in 1987 "Energy and Fuels", by the "Fuel Division" of the "American Chemical Society". A novelty has been the well-recognised publications of "IEA-Coal Research" in London, founded in 1975 by the IEA supported by IEA-Member Countries²².

A political issue that became of high priority in the seventies and eighties was the *protection of the environment*, the aims of which gave a lot of new impulses to coal science. Special attention was given to research into coal combustion with particular regard to the efficient use of coal as well as to the formation and abatement of all kind of pollutants and hazardous species. NO_x formation was found to be unexpectedly complicated and, therefore, of special scientific interest^{23,24,25}. Relevant investigations included research into the nature of nitrogen-compounds in the chemical structure of coal. Also, coal minerals and their „products“, ash and slag, in their different roles as sources of emissions, wastes or raw material for further use, won the interest of scientists. In the last decade the *protection of the earth's climate* has been an additional issue influencing coal science.

Interaction with other Sciences

Regarding its strong connection with chemistry, physics and chemical engineering, it is evident that every suitable progress was used for research on coal:

The exploration of chemical structure of coal has lead to comprehensive and well-defined results on the basis of developments of *spectroscopic methods* only. These are IR- and UV- spectroscopy and X-ray structural analysis in the 50s and 60s and the proton and solid state-NMR and the X-ray absorption spectroscopy in the last 20

years. *Thermal analysis* including Thermogravimetry (TGA) and Differential Thermal Analysis (DTA) had reached a technical status in the 60s that it became a reliable instrument for the investigations into coal pyrolysis, gasification, combustion and others. Small mass-spectrometers, IR-analysers and gas-chromatographs became routine tools for on-line gas analysis and completed these methods. The development of big *mass spectrometers* and an increasingly improved *hydrocarbon gas chromatography*²⁶ enabled coal scientists to make structural analysis. In order to investigate the porous structure of coal, char and coke methods have been developed since the beginning of the 30s already, to measure *porosity* and to characterise qualities and quantities of the *internal surfaces*. The most important ones are based on the work of Brunauer, Emmett and Teller²⁷ and Dubinin²⁸ introducing sorption of gases to characterise micropores and of Ritter and Drake²⁹ developing mercury intrusion for the characterisation of macropores. The enormous development of *microbiology and biotechnology* has opened the door for fundamentally new methods in coal science in the last decade³⁰. All of us experience the progress achieved by the development and application of *computers* and the useful algorithms available for data acquisition and evaluation and the possibilities of *modelling and simulation* of structures, reactions and reactors.

Chemical Structure and Structural Models

Attempts made in the first half of the century resulted hardly in saying much more with regard to chemical structure of coal than elementary analysis and qualitative hints to the main groups present in coal³¹. Later the dynamic development of spectroscopic methods allowed to analyse the products of the different destructive reactions with increasing precision and confidence. *Coal models* were proposed, in which the well-defined fragments were composed again taking into account the knowledge about structures and bonds in macromolecules. Given had made one of the first proposals³². Today's knowledge is based on quite a few ideas, which had been published among others by Wiser³³, Wender³⁴ and Shinn³⁵. Their basic assumptions and their main characteristics are reviewed e. g. by Davidson³⁶, and more recently by Haenel, Collin and Zander^{37,38}. Experiments on coal swelling in organic solvents suggested a 3-dimensional structure. Spiro has given notice to this by vivid space models³⁹. Of importance is the discovery of "guest molecules", hosted by the network, forming the "*mobile phase*"⁴⁰. The progress achieved in the past two decades, has confirmed and completed the picture convincingly. The NMR-studies as performed by the group lead by Pugmire⁴¹ and the investigations into nitrogen functionalities by Burchill and Welch⁴² shall be mentioned here as good examples. - The models have been utilised with great success to investigate the mechanisms of pyrolysis, hydrogenation and hydrocracking reactions including the formation of the products and its control by experimental conditions and catalysts.

Reactions based on Bond Cleavage

On the basis of the chemical structure model of coal Jüntgen has developed a reaction scheme for the *mechanism of coal pyrolysis*⁴³. Primary breaking of weaker bonds between the aromatic units followed by cracking, hydrogenation or agglomeration resulting in gas, condensable liquids, and char. The coal model and the reaction scheme based on it demonstrate its power in the conclusive explanation of the influence of experimental conditions like rate of heating, pressure and presence of hydrogen, on the distribution and the quality of the products⁴⁴. This progress has opened the door also for the simulation of pyrolysis by computer modelling. Using the

results on the macromolecular structure Pugmire⁴⁵, Solomon⁴⁶ and Niksa⁴⁷ each have developed and successfully tested relevant *models*. They predict the pyrolytic behaviour of different coals including the yields of the products at different conditions. The reaction mechanism of *direct coal liquefaction* is almost identical to that of pyrolysis. A scheme published by F. Derbyshire demonstrates the similarities⁴⁸.

To describe the kinetics of the products' formation H. Juentgen, K. H. van Heek⁴⁹ and co-workers have developed equations, considering the thermal bond-breaking rate determining step, this being the prelude of the non-isothermal kinetics of coal pyrolysis^{50,51}. The equations derived are used for the description of the curves measured and result in kinetic data. The *non-isothermal kinetics* has been used widely to describe and evaluate thermal reactions with solid fuel, for reactor simulation e. g. of gasifiers and furnaces. Over and above that coal science has developed a sturdy method for the evaluation of experimental data, a tremendous enrichment of thermal analysis in general.

Physical Structure of Char and Coke and Heterogeneous Reactions

Coke and char have a distinct *porous structure*⁵² reaching down into the dimensions of the molecular units. Important contributions to explain the development of inner surfaces under thermal treatment have been made by H. Marsh, A. Oberlin and others^{53,54,55}. Concerning the heterogeneous gas-solid-reactions literature till the 30s contains mainly stoichiometric and thermodynamic calculations. Kinetic studies on combustion starting in the third decade were performed on "pure carbons" such as "spectric coal" or graphitic material. The important work of Hottel⁴ has been mentioned. His results were further evaluated by Essenhigh and Howard⁵⁶, thereby acknowledging its importance for the understanding of *combustion kinetics*. A detailed theory describing the reactions in the different regimes was developed by Wicke, Hedden and Rossberg⁵⁷ in the 40ies and 50ies..

Char and coke from different natural coal or lignite, mainly investigated in the last 30 years, show enormous differences in *gasification rates*^{58,59}. The high reactivity of lignite chars is due to the catalytic influence of earth-alkalis, in particular Ca⁶⁰. Chars from coal treated below 1000°C have a medium reactivity, whereas high-temperature-coke shows distinctly lower values. To investigate the influence of temperature during or after pyrolysis P. L. Walker and co-workers at Pennsylvania State University, USA, made essential experiments leading to significant interpretations⁶¹. - Coal research since long was looking for interactions between amount, properties and accessibility of internal surfaces of char and coke and their reactivity⁶². A simple correlation between total area and reactivity does not exist in general. But the assumption of the existence of special configurations on char/coke surfaces, the "*active centres*", which react preferentially, was carrying on decisively.^{63,64,65}

Concluding Remarks

The fundamental knowledge about origin, properties and reactions of coal, their characterisation with respect to scientific or industrial use, and the manifold skills and methods for the treatment of coal related scientific problems hitherto has contributed in many ways and often unseen to the development of efficient and clean coal technologies. But many excellent and promising results got stuck also in the attempt to transfer them into practice, remaining unfulfilled dreams of the researcher, examples are hydrogasification, catalytically aided

gasification, or hydropyrolysis. Even if nowadays coal is world-wide preferably used for electricity production and coke making, we can be pretty sure, that knowledge gained in the fields of liquefaction, gasification and pyrolysis, will become necessary for industrial processes, possibly soon, as inexpensive oil and gas will not last forever and will not be equally accessible for every country. The predictions of the Club of Rome since 1972 are valid generally, even if the chronological order has had to be shifted somewhat into the future. Thus, as a global view, new and especially improved processes for the clean utilisation of coal remain to be a steady task for coming generations of coal scientists and engineers. science and technology will start from there and other developing countries in the future.

References

- ¹ J. Ivon Graham, H. G. Shatwell, Fuel 2, 1923, p. 54
- ² P. Feiler, Die Wirbelschicht, (The fluidised bed) Schriftenreihe des Firmenarchivs der BASF, Ludwigshafen, Germany, 1972
- ³ F. Fischer, H. Tropsch, Ber. Dtsch. Chem. Ges. 59, 1926, p. 830
- ⁴ C. M. Tu, H. Davis, H. C. Hottel, Ind. Eng. Chem. 26, 1933, p. 749
- ⁵ J. M. Beer, J. B. Howard, J. P. Longwell, A. F. Sarofim, Combustion and Flame 117, 1999, p. 1
- ⁶ Hottel, H. C. and Howard, J. B., New Energy Technology, MIT Press, Cambridge, Mass. 1971
- ⁷ Clean Fuels from Coal, Sept. 10-14, 1973 - Symposium Papers, Institute of Gas Technology, Chicago
- ⁸ Nuclear Engineering and Design, Special Issues: High Temperature Reactor for Process Heat Applications, 1975, p. 34 and 1984, p. 78,
- ⁹ Kugeler, K., Neis, N. and Ballensiefen, G. Eds., Fortschritte in der Energietechnik, (Progress in Energy Technology) Monographien des Forschungszentrum Jülich, Bd. 8, 1993
- ¹⁰ van Heek, K. H., Jüntgen, H. and Peters, W., J. of the Inst. of Fuel, 1973, p. 249
- ¹¹ Falbe, J., Chemierohstoffe aus Kohle, (Chemical Feedstock from Coal), G. Thieme Verlag, Stuttgart, Germany, 1977
- ¹² Proceedings International Conference on Coal Science, Düsseldorf, Germany, 7-9. 1981, Verlag Glückauf Essen, 1981
- ¹³ 1983 International Conference on Coal Science, Proceedings, Pittsburgh, USA, August 15-19, 1983
- ¹⁴ Proceedings 1985 International Conference on Coal Science, 28-31 October 1985 Sydney, N. S. W., Pergamon Press, Sydney 1985
- ¹⁵ Moulijn, J. A., Nater, K. A., and. Chermin, H. A. G., Eds., 1987 International Conference on Coal Science, Maastricht, The Netherlands, Oct. 26-30, 1987, Proceedings, Coal Science and Technology 11, Elsevier, Amsterdam, 1987
- ¹⁶ 1989 International Conference on Coal Science Proceedings Vol. I, II, October 23-27, 1989, Tokyo, Japan
- ¹⁷ 1991 International Conference on Coal Science Proceedings, 16-20 September 1991, Newcastle, U. K. Edited by the Int. Energy Agency Coal Research Ltd., Butterworth Heinemann Oxford 1991
- ¹⁸ Michaelian, K. H. Ed., International Conference on Coal Science, September 12-17, 1993, Banff, Alb. Canada, Conference Proceedings Vol. I, II, ISBN- 0-9697498-0-5
- ¹⁹ Pajares, J. A. and Tascon, J. M. D. Eds., Coal Science, Proceedings of the Eighth International Conference on Coal Science, Oviedo, Spain, Sept. 10-15, 1995, Vol. I, II, Coal Science and Technology 24, Elsevier Amsterdam, 1995
- ²⁰ Ziegler, A., van Heek, K. H., Klein, J. and Wanzl, W. Eds., Proceedings 9th International Conference on Coal Science, 7-12. 9. 1997, Essen Germany, Vol. I, II, III, DGMK Tagungsbericht 9702, ISBN -931850-20-X3
- ²¹ Bao Qing Li, Zhen Yu Liu, Prospects for Coal Science in the 21st Century, Proc. 10th ICCS, Shanxi Science & Technology Press, Taiyuan, China, 1999
- ²² IEA Coal Research The Clean Coal Centre, Annual Report 1997-1998, ISBN 92-90029-309-8
- ²³ Pohl, J. H. and Sarofim, A. F., Devolatilisation and oxidation of coal nitrogen, 16th Symp. on Combustion, The Combustion Institute, 1976, p. 491
- ²⁴ de Soete, G. G., Rev. Gen. Therm. Fr., 1989, No. 330-331, p. 353
- ²⁵ Wojtowicz, M. A., Pels, J. R. and Moulijn, J. A., Fuel, 1995, 74, p. 507
- ²⁶ A. G. Sharkey Jr, Spectrometry of Fuels, Plenum Press, New York, 1970
- ²⁷ S. Brunauer, P. H. Emmett, E. Teller, Journal of the American Chemical Society 60, 1938, p. 309
- ²⁸ M. M. Dubinin, Chemistry and Physics of Carbon 2, Marcel Dekker New York, 1966, p. 51
- ²⁹ H. L. Ritter, C. L. Drake, Ind & Eng. Chemistry. Analytical Edition 17, 1967, p. 782
- ³⁰ Klein, J. et al., Coal in Biotechnology in Rehm H.-J. and Reed, G. Eds. Biotechnology Vol. 6b, VCH Verlagsges. Weinheim, 1988, p. 499
- ³¹ H. H. Lowry, Ed., Chemistry of Coal Utilisation I, II, John Wiley & Sons New York, 1945, 1947
- ³² P. H. Given, Fuel, 39, 1960, p. 147
- ³³ W. H. Wiser, Proc. EPRI Conf. Coal Catalysis Santa Monica, Cal., 1973
- ³⁴ I. Wender, Chemical Reactions and the Constitution of Coal in Chemistry of Coal Utilization, 2nd Suppl. Ed. M. A. Elliott, J. Wiley & Sons New York, 1981, p. 520
- ³⁵ J. H. Shinn, Fuel, 63, 1984, p. 1187
- ³⁶ R. M. Davidson, Molecular Structure of Coal, IEA Coal Research, 1980
- ³⁷ M. W. Haenel, G. Collin, M. Zander, Erdöl Erdgas Kohle 105, 1989, p. 71
- ³⁸ M. W. Haenel, Fuel, 71, 1992, p. 1211
- ³⁹ C. L. Spiro, Fuel 60, 1981, p. 1121; Fuel 61, 1982, p. 1080
- ⁴⁰ P. H. Given, A. Marzek, W. A. Barton, L. J. Lynch, B. C. Gerstein, Fuel 65, 1986, p. 155
- ⁴¹ M. S. Solum, R. J. Pugmire, D. M. Grant, Energy & Fuels, 3, 1989, p. 187
- ⁴² P. Burchill, L. S. Welch, Fuel, 68, 1989
- ⁴³ H. Jüntgen Fuel 63, 1984, p. 731
- ⁴⁴ K. H. van Heek, W. Hodek, Fuel 73 1994, p. 886
- ⁴⁵ T. H. Fletcher, A. R. Kerstein, R. J. Pugmire, M. S. Solum, D. M. Grant, Energy & Fuels 6 1992, p. 414
- ⁴⁶ P. R. Solomon, D. G. Hamblen, M. A. Serio, S. Charpenay, Fuel 72 1993, p. 469
- ⁴⁷ S. Niksa, Combustion & Flame 100, 1995, p. 384
- ⁴⁸ F. Derbyshire et al. ULLMANN'S Encyclopaedia of Industrial Chemistry, Vol. A7, 1986
- ⁴⁹ H. Jüntgen, Erdöl und Kohle, 17. 1964, p. 180
- ⁵⁰ H. Jüntgen, K. H. van Heek, Fuel 47 1968, p. 103
- ⁵¹ H. Jüntgen, K. H. van Heek, Fuel Processing Technology 2, 1979, p. 261
- ⁵² J. W. Patrick Ed., Porosity in Carbons, Edward Arnold, London 1995
- ⁵³ H. Marsh, E. A. Heintz, F. Rodrigues-Reinoso, Eds., Introduction to carbon tech., Univ. of Alicante, 1997
- ⁵⁴ H. Marsh, Carbon 29, 1991, p. 703
- ⁵⁵ A. Oberlin, in Chem. and Phys. of Carbon, Ed. P. Thrower, Vol. 22, Marcel Dekker New York, 1989, p. 1
- ⁵⁶ R. E. Essenhigh, R. Froberg, J. B. Howard, Ind. Eng. Chem. 57, 1965, p. 33
- ⁵⁷ E. Wicke, K. Hedden, M. Rossberg, BWK, 8, 1956, p. 264
- ⁵⁸ K. H. van Heek, H. Jüntgen, W. Peters, J. of the Inst. of Fuel, 1973, p. 249
- ⁵⁹ K. H. van Heek, H. J. Mühlen, Fuel 64, 1985, p. 1405
- ⁶⁰ A. Linares-Solano, C. Salinas-Martinez, D. Cazorla-Amoros, J. P. Joly, in reference 55, p. 409
- ⁶¹ L. R. Radovic, P. L. Walker, R. G. Jenkins, Fuel 62, 1983, p. 849
- ⁶² N. M. Laurendeau, Prog. Energy Combust. Sc. 4, p. 221
- ⁶³ N. R. Laine, F. J. Vastola, P. L. Walker, Journal of Physical Chemistry, 67, 1963, p. 2030
- ⁶⁴ E. Hippo, P. L. Walker, Fuel 54, 1975, p. 245
- ⁶⁵ J. Lahaye, P. Ehrburger, Ed., Fundamental Issues in Control of Carbon Gasification Reactivity, NATO ASI Series E: Applied Sciences - Vol. 192, Kluwer Academic Publishers, Dordrecht 1991

Progress in Coal Liquefaction Including a Discussion of Wilsonville Data

Anthony M. Valente* and Donald C. Cronauer**

* BP Products North America Inc., Naperville, IL

** Argonne National Laboratory, Argonne, IL

ABSTRACT

Activity in direct coal liquefaction research has passed through a number of swings since its inception. High activity levels included Germany's production during WWII and research during the period of 1970 through 1992. A sizeable number of processes have been developed. Effort appears to have evolved toward a two-stage reactor concept with one or both stages containing active hydrogenation catalysts with supplemental and/or recycled mineral matter. A high point of research activity centered upon the Advanced Two-Stage Coal Liquefaction Facility located in Wilsonville, AL. A database was set up to correlate the effect of operating variables in their liquefaction of Illinois No. 6 seam bituminous coal. Overall preferred processing conditions for generating distillable liquids included the use of high reactor temperatures ($>430^{\circ}\text{C}$) and a high process solvent resid concentration ($>50\text{ wt}\%$ if mechanically possible). The space rate of coal in the reactors should be set at a point where resid production is minimized. Significant results included lower coal conversion, hydrogen consumption, $\text{C}_1\text{-C}_3$ yield, IBP-350EF yield, and $\text{C}_1\text{-C}_3$ selectivity when using half-volume over full-volume reactors at similar conditions, including space velocities. These were apparently due to flatter reactor temperature profiles and lower catalyst to thermal volume ratios.

INTRODUCTION AND BACKGROUND

Research in the field of liquefaction of coal has passed through a number of phases since its inception with coking to recover liquids and gases in the 1840's. Direct liquefaction which involved the extraction of coal with a solvent at high temperatures and pressures was patented in 1913 by Bergius and commercialized soon thereafter. Direct liquefaction in combination with other routes to generate liquids was the primary source of fuels in Germany during WWII.

Additional research for this route to liquids followed in the US and elsewhere in the 1950's. Effort and funding decreased into the late 1960's. In the early 1970's crude oil prices rose and availability decreased. At this time, essentially a panic occurred with the amount of funding almost exceeding the number of staff and research and development facilities. Effort peaked in the next decade, and it has now fallen to a low level again. The only remaining effort of a major scale is that of Hydrocarbon Technologies, Inc. (HTI) in combination with China; their work is being discussed by Dr. Peizheng Zhou in this session.

Starting with fundamentals, coal is a solid with a low level of hydrogen (4 – 6 wt%) while the desired product liquid contains 10 to 15% hydrogen. Coal contains a sizeable amount of mineral matter (3 to 20%) and water (5% with bituminous coal to 30+% with subbituminous and lignites). It also contains a wide range of oxygen (2% to 20+%, and organically-bound sulfur (0.2 to 5%). Its level of nitrogen averages about 1%. To generate refinery feedstocks, catalytic hydrogenation is necessary at some step in the process. Common catalysts are molybdenum or tungsten oxides on alumina promoted by cobalt and/or nickel; these catalysts are sulfided prior to use. The pore size distribution and structure of the catalyst are important.

Laboratory and academic research has centered upon chemical structures and reaction mechanisms. Various groupings of products have been reported, such as aromatics, aliphatics, asphaltenes, preasphaltenes, asphaltols, maltenes, etc. In most cases these fractions were dependent upon the separation or identification technique. As far as a refinery feedstock is concerned, emphasis was placed upon distillate cuts, hydrogen and heteroatom contents and solid (or coking) levels.

There are a number of processes available for the direct liquefaction of coal. At least 18 process concepts have been developed, many through pilot plant or semi-works scale operation. A good summary of these processes has been issued by the UK Department of Trade and Industry.¹

The overall process scheme is the following: 1. pulverized coal is mixed with coal-derived, recycled solvent; 2. the resulting slurry is reacted in one or more reactors at 350°C to 450°C (620K - 720K) for a period of about one hour or more; and 3. the resulting product is upgraded. The approach depends upon the type of feed coal, the desired characteristics of the product liquids, the availability of supplemental feed (hydrogen, carbon monoxide, treated solvents), solid separation schemes, gasification processes (by-product solids and/or gases), location and catalysts. To an extent, overall process development has evolved toward a two-stage route with one or both stages containing active hydrogenation catalysts with supplemental and/or recycled mineral matter.

COAL LIQUEFACTION RUNS AT WILSONVILLE, AL

An extensive series of liquefaction runs was made at The Department of Energy Advanced Two-Stage Coal Liquefaction Facility located in Wilsonville, Alabama. The facility was operated by Southern Company Services (SCS) with funding by the United States Department of Energy (DOE), the Electric Power Research Institute (EPRI), and Amoco Oil Corporation. The unit capacity was about 6 tons of coal per day. Operation occurred from 1970 through 1992. A description of the process and a summary of runs made using low rank coals have been reported.^{2, 3}

Liquefaction runs which were made with bituminous Illinois No. 6 coal are discussed herein to show the scope of coal conversion and the distribution of products that can be achieved. Emphasis was placed upon close-coupled, integrated two-stage liquefaction (CC-ITSL) mode with and without interstage separation and "ashy recycle." Ashy recycle refers to the recycle of a portion of the mineral matter and unconverted coal with the recycle solvent to the feed tank of the first reactor. This recycle increased coal conversion and liquid yield due to the catalytic activity of recycled pyritic iron in the coal minerals. Solids separation was achieved using a Kerr-McGee ROSE-SRITM unit, which was placed after the second reactor. For reference, coal conversion and yields were reported on a basis of weight per unit of MAF (moisture ash free) coal.

The addition of a supported catalyst in either the first or second stage or both stages was also studied at Wilsonville. All the runs using Illinois No. 6 seam coals in the close-coupled mode were made with a supported catalyst in either the second stage only (thermal/catalytic or T/C) or in both stages (catalytic/catalytic or C/C). The format in which the Wilsonville pilot plant data was reported has changed over the years. A database design for runs in CC-ITSL mode was developed in order to standardize their data. All runs at the Wilsonville pilot plant have been made in close-coupled mode since 1985 and Illinois No. 6 seam coal has been used in more of these recent runs than any other single coal.

The database consisted of sixteen process variables that were used in a linear regression analysis of unit conversions and yields. Due to the recycle of high boiling liquids to form the coal slurry to the first stage, the two stages were interrelated. The products of the

first stage influenced the products of the second stage and vice versa. For this reason, the focus of this work is on the two-stages as a single unit.

The model suggested that the most influential variables are reactor temperatures, coal space rate, each stage's catalyst age, and process solvent resid concentration. Use of half-volume reactors caused lower C1-C3 yield, IBP-350F yield, C1-C3 selectivity, coal conversion, and hydrogen consumption. This was likely due to the lower catalytic/thermal volume ratio and flatter temperature profile of the half-volume versus the full-volume reactors.

From these models and correlations, an estimate of the optimum conditions for liquefaction of Illinois No. 6 coal was made. The regression equations suggested that increasing temperature in both stages increased the distillable liquid production and increased resid conversion. For reference, the temperature effects in both reactors were similar and essentially overlapped, so only that of the First Stage is included herein as Fig. 1. As the temperatures increased, there was a loss of a distillate product due to gas production; however, the production of distillable liquids increased more than the C1-C3 gas make. A plateau where higher temperatures cause no increase in a distillate liquid yield and an elevated gas make would likely be reached. Wilsonville, however, did not demonstrate this point of diminishing liquid yields. Minimizing the catalyst age (and increasing catalyst replacement) showed improvement in yields (Fig. 2). The yields of hydrocarbon gases and 350-450F liquids did not change significantly as the catalyst age increased. This observation implies that the formation of low boiling hydrocarbons was primarily thermal.

The optimum coal space rate was difficult to surmise. Coal conversion was a very weak function of a space rate (Fig. 3). If converting coal to liquids is the primary goal, then the space rate of coal can be increased significantly from that demonstrated at Wilsonville. The amount of low boiling products would suffer. As space rate was increased, the amount of resid became significant. If an all distillate product slate (no resid production) is desired, then the space rate should be pushed higher at given conditions until resid is produced. At the base conditions shown in Fig. 3, this would be around 35 lb/hr* ft^3 .

Process solvent resid concentration should be increased to the operability limit. Recycling more resid allows more to convert to distillable liquids, as shown in Fig. 4. Coal conversion also showed a marginal increase as resid concentration in the recycle solvent was increased.

The regression models showed that the Wilsonville reactors when run at half-volume generally demonstrated lower C1-C3 yield, IBP-350F yield, coal conversion, and hydrogen consumption. Distillate yield was, however, not significantly affected by using half-volume reactors. The half-volume reactors exhibited better internal mixing and would thus be more similar to a commercial reactor than full-volume reactors.

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REFERENCES

1. Dept. of Trade & Technology, UK, Coal Liquefaction: Technology Status Report 010, Oct. 1999 (See www.dti.gov.uk/ent/coal)
2. Lamb, C. W., Nalithan, R. V., Johnson, T. W., PREPRINTS: ACS Div. Fuel Chem., 1986. 24, 1091.
3. Munkvold, G., Valente, A. M., Cronauer, D. C., PREPRINTS: ACS Div. Fuel Chem., 1994. 39(1), 92.

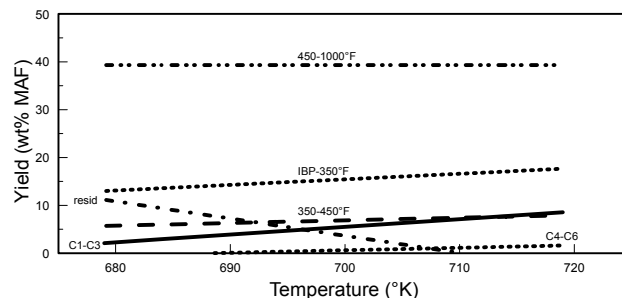


Figure 1. Reactor No. 1 Temperature Effect on Yields

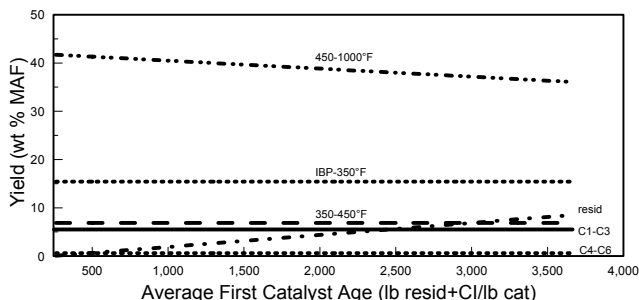


Figure 2. Effect of Reactor No. 1 Catalyst Age on Yields

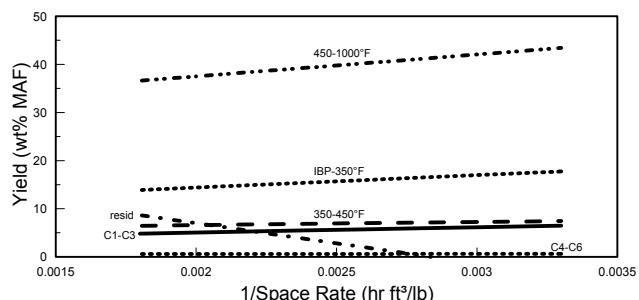


Figure 3. Inverse Space Rate Effect on Yields

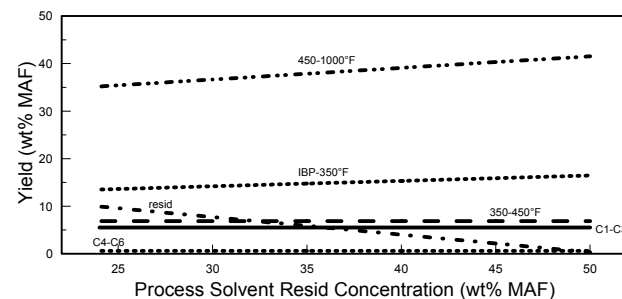


Figure 4. Recycle Resid Concentration Effect on Yields

AN ANALYSIS OF THE ACCOMPLISHMENTS OF THE DOE DIRECT COAL LIQUEFACTION PROGRAM, 1976-2000

^(a) R. A. Winschel and F. P. Burke
^(b) D. Gray and G. Tomlinson

(a) CONSOL Energy Inc., Research & Development,
4000 Brownsville Road, South Park, PA 15129
(b) Mitretek Systems, 3150 Fairview Park Drive South
Falls Church, VA 22042-4519

Summary

The DOE direct coal liquefaction program, conducted between 1976 and 2000, resulted in the development and optimization of a commercially ready technology for the production of petroleum substitutes as refinery feedstocks. An intensive large scale demonstration program in the late 1970s and early 1980s demonstrated overall engineering feasibility. Subsequent process research and development work overcame the major technical and economic obstacles to commercialization of the process. As a result, direct liquefaction products that meet or exceed crude oil qualities can be made for about \$30/bbl. The technology was shown to be applicable to a wide range of coals in the United States. Fundamental research supported the process development effort, and provided direction in optimizing process performance. The DOE program met the goal of defining the costs and benefits of direct coal liquefaction as a strategic alternative to imported oil as a source of liquid fuels and petrochemicals.

Introduction

To understand the costs and benefits of the DOE direct coal liquefaction effort, it is important to recognize that the program consisted of three main components. The first was the relatively large-scale demonstration of thermal/catalytic hydrogenation processes (referred to below as "Phase I" processes) in the 1970s and early 1980s. These demonstrations were done to accelerate the availability of coal liquefaction technology as a short-term response to the energy crisis of the 1970s. The second component was a more fundamental research program to investigate potential improvements in the thermal/catalytic processes, and to identify potential alternative processes, based on a better understanding of coal and process chemistry. The third component was a broadly based bench-scale and pilot plant process development program to overcome the technical and economic deficiencies encountered in the earlier Phase I demonstration programs. The processes developed in this third component of the program are referred to below as "Phase II" processes.

In 1976, U.S. petroleum imports cost \$106 billion (in 1999 dollars), and during the period from 1976 through 1999, the U.S. imported 68 billion barrels of crude oil, at a cost of \$2 trillion (1999 dollars). Between 1976 and 1999, the average cost of a barrel of crude oil, in 1999 dollars, has been \$29. The overall cost of the DOE direct coal liquefaction program, through the year 2000, was \$3.6 billion (1999 dollars), or 0.2% of the imported petroleum cost. As shown in Figure 1, 89% of the total DOE spending occurred between 1976 and 1982. The majority was spent on large plants to demonstrate the Phase I processes. The DOE investment was matched by substantial investments by private industry, state governments, and academic institutions.

In the early 1970s, in a military and international political climate much different than today's, the United States was faced with a shortfall in supplies of petroleum which it was unable to satisfy with domestic sources. The gasoline supply situation was

particularly visible and acute, but the electric power industry, which had increased petroleum consumption by 600% between 1963 and 1973, also was seeking reliable domestic oil sources. In an attempt to ensure alternatives to imported oil, a national decision was made to pursue direct coal liquefaction, among other options, as a means to produce domestic supplies of transportation and utility fuels.

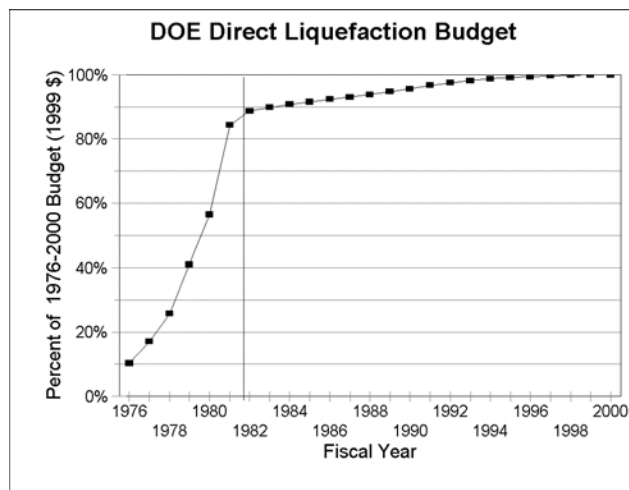


Figure 1. DOE Direct Liquefaction Budget.

The major oil companies (Exxon, Mobil, Chevron, Amoco, Conoco, Gulf and others) and the electric power industry (notably Electric Power Research Institute (EPRI) and Southern Company) actively supported this decision as evidenced by their substantial investment in the development and demonstration of direct liquefaction technology. The majority of the funding in the Phase I direct liquefaction program of the 1970s and early 1980s was focused on large projects to develop and demonstrate the Exxon Donor Solvent (EDS), the Hydrocarbon Research Inc. (HRI) H-Coal and SRC-II distillate fuels processes, and the Solvent Refined Coal (SCR) boiler fuel process.

Concurrently, a much smaller, but significant amount of funding was directed to the universities, private sector and government labs which conducted more fundamental research to determine if better alternatives to the high temperature thermal/catalytic processes like EDS and H-Coal could be identified for further development. This work involved substantial research on the chemistry of coal and associated products.

While the H-Coal and EDS programs demonstrated the technical and engineering feasibility of direct coal liquefaction, many issues were not satisfactorily resolved, including those of process yield, selectivity, product quality, and, ultimately, economic potential. However, process development research had identified a number of options for process improvement that were further developed and demonstrated at the bench and pilot plant scale, principally at Lummus-Crest, HRI (later, Hydrocarbon Technologies Inc. (HTI)) and the Wilsonville facility, during the 1980s and early 1990s. This Phase II development work successfully addressed the outstanding technical issues identified earlier, and largely optimized the process in terms of the most important performance parameters. The principal accomplishments of the program are described below.

Discussion

High Yields of Distillate Fuels Demonstrated. One of the most important accomplishments of the Phase II work was a substantial increase in liquid yields compared to the Phase I processes. High liquid yield is important, because direct liquefaction

is capital-intensive. Therefore, increasing liquid yields greatly reduced the capital cost component of the process on a dollars/barrel/stream day basis. As shown below, liquid fuel yields were increased from 45% to 50% (MAF coal basis) for Phase 1 processes to about 75% (more than 4.5 bbl/t of MAF coal) for Phase 2 processes, while the yields of less valuable gaseous and non-distillate fuels were reduced commensurately, as shown below for mid-western U.S. (Illinois Basin) coal. In the table, ITSL refers to Integrated Two Stage Liquefaction, and CMSL refers to Continuous Multi-Stage Liquefaction.

Table 1. Process Yields with Illinois Basin Coal

Process Year	SRC-II 1980	H-Coal 1981	EDS early 80s	ITSL 1989	CMSL 1994
<u>Yield, wt % MAF Coal</u>					
Heterogases	12.9	11.3	17.4	15.2	15.2
C ₁ -C ₃ gas	14.5	12.8	19.0*	5.4	11.4
Naphtha	19.3	22.9	22.8	14.5	20.7
Middle Distillate	25.2	20.0	17.0	21.7	39.1
Gas Oil	4.9	7.6	4.4	29.6	12.5
Total Distillate	47.3	50.5	44.2	65.8	72.3
H Consumption, wt %	5.0	6.0	5.9	6.0	7.5
H Efficiency, lb dist./lb H Consumed	9.5	8.4	7.5	11.0	9.7
* C ₁ - C ₄ gas					

High-Quality Liquids Produced. The liquids made in the Phase I processes were intended to be crude oil replacements, but they were unstable, highly aromatic, and had high heteroatom (sulfur, nitrogen, oxygen) contents. This prompted concern about refinability, storage stability, and human health, principally related to carcinogenicity. In the Phase II work, considerable attention was paid to improving liquid fuel quality. The Phase II process produces liquid fuels containing no resid, no metals, and very low levels of heteroatoms. These primary products could be refined in conventional refineries to meet then-current specifications for motor and turbine fuels. Product quality evaluations, which were an important element of the Phase II work, ensured that acceptable transportation fuels can be produced by direct coal liquefaction. The Phase 2 processes make a superb quality naphtha that can be processed in conventional refineries into high-quality gasoline. No undesirable blending interaction with conventional gasolines and naphthas is expected. Direct coal liquefaction middle distillates can serve as blend stocks for the production of diesel fuel and kerosene. The higher hydrogen contents of Phase 2 process products alleviate the carcinogenicity concerns related to Phase 1 process products. The properties of naphthas generated by Phase 1 and Phase 2 processes are compared in Table 2.

Table 2. Comparison of Properties of Naphthas Generated by Phase 1 and 2 Processes

Process Year	Illinois Basin Coal				PRB Coal On-Line Hydrotreater
	SRCII 1980	H-Coal 1981	EDS Late 70s	CMSL 1996	CMSL 1996
<u>Naphtha Properties</u>					
b.pt., °F	100-400	180-380	158-392	ibp-350	70-350
°API	39	35	31.1	49.9	53.5
H, wt%	11.5	11.6	10.9	14.0	14.7
S, wt %	0.2	0.2	0.5	0.04	0.02
N, wt %	0.4	0.31	0.2	0.02	0.002
O, wt %	3.9	3	2.8	0.3	<0.1

Process Scale-Up Demonstrated. The Phase I work demonstrated successful continuous operation of plants as large as 200 t/d of coal feed. The Phase II processes are sufficiently similar to the

Phase I processes, in terms of process equipment and unit operations, that this experience is directly applicable. In addition, some of the key process equipment, such as the ebullated-bed reactor, is used in petroleum refineries around the world. Materials of construction and equipment designs were found to overcome corrosion, erosion, and fouling problems experienced in Phase 1 plants; these new materials and designs were demonstrated to be suitable. As a result, we can approach the scale-up of the Phase II processes to commercial scale with reasonable confidence. Some specific issues that were originally problem areas, but that were overcome by improved materials, equipment, or process design during the development program include: deashing, product compatibility with conventional fuels, let-down valve erosion, preheater coking, and corrosion in distillation columns. This list is illustrative, rather than comprehensive.

Direct Liquefaction Shown to Apply to a Wide Range of Coals. Lignite, subbituminous, and bituminous coals from the eastern, mid-western, and western U.S. were shown to be suitable feedstocks. These represent the vast majority of U.S. coal resources. One important development was the application of direct liquefaction to low rank coals. In the 1970s, it was generally believed that subbituminous coal was an inferior liquefaction feedstock because of its high oxygen content, and perceived lower reactivity. One emphasis of the Phase II work was to apply direct liquefaction to low-rank coals. This is important, because it proved that the huge reserves of inexpensive western U.S. subbituminous coals make excellent liquefaction feedstocks. The Phase 2 work showed that direct liquefaction is a flexible process. It was shown that direct liquefaction could be applied to a mixed feedstock containing coal and petroleum resids, heavy oil, or bitumen ("coprocessing"), and to coal and waste polymers. This allows a single plant to operate with the most economical feedstock available at a given place and time. The improvement in liquid yields of the Phase 2 processes, relative to Phase 1 processes, with U.S. Powder River Basin subbituminous coal is shown in Table 3.

Table 3. Process Yields with Powder River Basin Coal

Process Year	H-Coal 1980	ALC/CMSL 1996
<u>Yield, wt % MAF Coal</u>		
Heterogases	19.8	21.3
C ₁ -C ₃ gas	11.0	12.4
Naphtha	24.3	23.0
Middle Distillate	14.5	9.7
Gas Oil	11.9	33.4
Total Distillate	50.7	66.1
H Consumption, wt %	5.6	6.8
H-Efficiency, lb dist./lb H consumed	9.0	9.7

Economic Competitiveness Was Significantly Improved.

Table 4 shows the economic analysis of conceptual full-scale plant designs employing three levels of technological development. The plants have been analyzed on the basis of a common set of economic assumptions shown below.

Return on Equity	15%	Federal Tax Rate	34%
% Equity	25%	State/Local Property Tax	1%
Loan Interest (16 yr)	8%	Depreciation, DDB, yr	16
Construction Period, yr	4		

Table 4. Economics of Coal Liquefaction

	H-Coal		ITSL	
	1981 \$	1999 \$	1991 \$	1999 \$
Hydrogen Source	Coal	Coal	Coal	Coal
Yield, bbls/day	50,000	50,000	69,000	69,000
Coal Feed, T/D AR	26,370	26,370	25,415	26,415
at \$/Ton AR	20.5	20.5	20.5	20.5
Plant Cost \$MM	\$2,769	\$4,592	3,543	\$4,239
Escalation Factor		1.658		1.197
Capital Cost/@ \$MM/yr	\$415	\$689	\$531	\$636
Coal Cost, \$MM/yr	\$178	\$178	\$172	\$172
O&M, \$MM/yr	\$111	\$184	\$115	\$138
Total Cost/yr	\$705	\$1,051	\$819	\$946
MM bbls/yr	16.50	16.50	22.77	22.77
RSP	\$42.70	\$63.69	\$35.95	\$41.53
Premium	1.00	1.00	1.07	1.07
Eq Crude RSP	\$42.70	\$63.69	\$33.60	\$38.81
Capital/Barrel/Day		\$91,841		\$61,439
	CMSL			
	1994 \$	1999 \$	1999 \$	1999 \$
Hydrogen Source	NG	NG		Coal
Yield, bbls/day	51,500	51,500		51,500
Coal Feed, T/D AR	13,400	13,400		18,090
at \$/Ton AR	20.5	20.5		20.5
Plant Cost \$MM	\$2,481	\$2,714		\$2,914
Escalation Factor		1.094		
Capital Cost/@ \$MM/yr	\$372	\$407		\$437
Coal Cost, \$MM/yr	\$91	\$91		\$122
Natural Gas, \$MM/yr	\$71	\$71		
O&M, \$MM/yr	\$74	\$81		\$87
Total Cost/yr	\$609	\$651		\$647
MM bbls/yr	17.00	17.00		17.00
RSP	\$35.81	\$38.28		\$38.06
Premium	1.20	1.20		1.20
Eq Crude RSP	\$29.90	\$31.96		\$31.78
Capital/Barrel/Day				\$56,580

All plants employ Illinois 6 coal. The first design, designated H-Coal, is based on an analysis by process developers in 1981.¹ Capital required for a first of a kind plant employing H-Coal technology was estimated at \$3.258 billion 1981. We have reduced this figure by 15% to reflect an Nth plant, consistent with the other estimates in Table 4.

The second plant, designated ITSL is based on a detailed preliminary design prepared for DOE by Bechtel in 1991-92.² Performance assumed in that study was derived from test results from run 257 at the Wilsonville Pilot Plant.

The plant designated as CMSL is based on bench scale results at HTI. Capital and operating costs are based on preliminary designs prepared by HTI in 1997.³ The HTI design uses natural gas as a feedstock for some hydrogen production. The design has been modified for coal only input in order to be compatible with the other plants.

Table 4 shows that the Required Selling Price (RSP) of direct liquefaction products on an equivalent crude basis to be about \$64, \$38, and \$32 per barrel for H-Coal, ITSL, and CMSL respectively. Figure 2 shows the contribution of coal, O&M, and capital related charges to the total RSP.

The principal advantage of ITSL vs. H-Coal stems from the substantial increase in yield per ton of coal processed. This, plus improvements in gasification and gas treatment, results in an improvement in yield of about 20% while reducing capital costs by over 5%. Capital cost per daily barrel was reduced from \$91,800 to \$61,400 (in 1999 dollars).

CMSL technology permits a further reduction in capital cost per daily barrel to \$56,600. Some additional savings would result if the plant were scaled to the higher coal input of the other plants shown.

CMSL employs less complex reactors and has much reduced catalyst costs. Total catalyst and chemical costs are less than \$500/daily barrel of capacity vs. \$1,160 for the Bechtel ITSL design. The major advantage of CMSL is improved product quality. Syncrude quality considerations are discussed below.

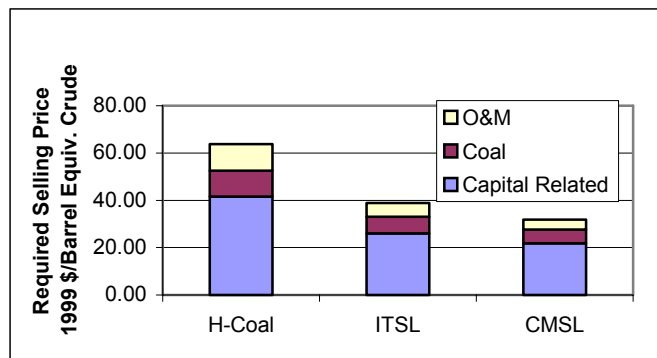
**Figure 2.** Components of Syncrude RSP.

Table 5 compares the quality of syncrudes from the three configurations to a typical U.S. crude oil. H-Coal liquids were characterized by low hydrogen content and other limitations noted earlier in this report. These limitations counterbalanced their advantage of being all distillate materials that produced a considerable volume gain when refined. The assessment in Table 5 that they had a value to refiners equal to crude (e.g., premium of 1.0) may be optimistic.

Table 5. Properties of Syncrude and Typical Crude

	H-Coal	ITSL	CMSL	Typ. Crude
Carbon, wt %	86.63	85.72	86.57	85.80
Hydrogen, wt %	10.54	11.48	13.08	13.00
Nitrogen, wt %	0.50	0.49	44 ppm	2000 ppm
Sulfur, wt %	0.19	0.07	0.06	1.00
Oxygen, wt %	2.13	2.24	0.44	
Vanadium, ppm	nil	nil	nil	200
650 °F ⁻ , wt %	83	79	80	53
975 °F ⁺ , wt %	0	0	0	20
Gravity, °API	27	22	38	32
Premium	1.00	1.07	1.20	1.00

ITSL products are more similar to petroleum and thus more easily processed. The premium of 1.07 relative to crude oil was determined by Bechtel through extensive refining analysis using the PIMs model.

CMSL liquids contain no residual material and only limited amounts of material boiling above 750 °F. The premium value of 1.2 relative to crude was assessed by HTI in the referenced study.³

Production of Higher Value Chemical Co-Products Demonstrated. Direct coal liquefaction is particularly well suited to the co-production of certain chemicals, many of which preserve the inherent molecular structure of the original coal. The production of cresylics, paraffin wax, sulfur (or sulfuric acid), and ammonia co-products was demonstrated. The Phase 2 process operated with subbituminous coal can yield 9% MAF of mixed cresylics (valued at \$0.55/lb, 1999) and 4% MAF of paraffin wax (valued at \$0.37/lb, 1999, fully refined). Benzene, toluene, BTX, other aromatics, argon, krypton, nitrogen, and other specialty chemicals also can be co-produced with liquid fuels. A coal liquefaction plant dedicated to producing chemicals, rather than fuels, and integrated into an Integrated Gasification Combined Cycle (IGCC) plant could be operated at less severe conditions and at substantially less cost than a stand-alone

liquefaction plant. This suggests the possible inclusion of a direct liquefaction module in a Vision 21 facility. "Vision 21" refers to DOE's conceptual facility of the future that produces some combination of electric power, clean fuels, and chemicals, with essentially no emissions of pollutants and reduced emissions of carbon dioxide.

Benefits Derived from Fundamental Research Program. A research program, conducted concurrently with the Phase 1 and Phase 2 development programs, evaluated novel process concepts and the fundamental chemistry of coals and catalysts and developed suitable analytical methodology. This program led to better understanding of the process. Some of this understanding, such as the benefits of slurry catalysis, was incorporated in the process development effort that generated the Phase 2 process. This work was sufficiently extensive to conclude that the catalytic/thermal direct liquefaction process, as developed with DOE, is the best liquefaction pathway, and that radical departures are unlikely to result in substantially improved processes. Thus, much of the value in the work was in providing indirect confirmation that the process development was near-optimum. The analytical techniques, catalyst development, and catalyst testing methodologies have spin-off value in that they are being applied in other fields or are likely to be in the future.

Conclusions

The DOE direct liquefaction program produced a reasonably mature technology. The intensive effort between 1976 and 1982 (Phase I), when 90% of the program funds were expended, resulted in a demonstration of the technical feasibility of the major process components. The Phase I processes, however, were deficient in terms of product yield and quality. This stimulated further research and development work between 1983 and 1999 (Phase II). The Phase II work was significantly less costly than the earlier demonstration projects, but resulted in substantial improvements in process performance and economics. It now is possible to produce liquids of high quality at yields that approach the theoretical maximum. At the same time, the cost for a barrel of product dropped by 50%, because of process optimization and increased yields. Economic and engineering studies conducted throughout Phase II have reduced the uncertainty and, therefore, the risk associated with commercial deployment of the technology. Many ideas for improving the basic thermal/catalytic process were identified and evaluated. Some of these were incorporated into the process development effort. In addition, considerable research was directed toward a better fundamental knowledge of coal chemistry, and to identify and explore novel liquefaction concepts distinct from the thermal/catalytic processes. The knowledge gained in the fundamental investigations is valuable in assuring that direct liquefaction technology, as it has been developed, represents a likely optimum in terms of process performance and costs. This knowledge would not have been available without the persistent advances in the technology achieved in the DOE direct liquefaction program.

The current technology is well defined in terms of cost and performance. It represents a technically available option for the production of liquid fuels. It can be used domestically in the United States to limit our exposure to oil price increases in the international market or to offset supply reductions. It also can be used by other nations who choose to use domestic coal to meet their transportation fuel needs, thus reducing demands on conventional petroleum sources. It can be used with coal alone, or to co-process a variety of lower value feedstocks. The results of the DOE program allow direct coal liquefaction to be accurately assessed in context to the costs and risks associated with other options for securing liquid fuel supplies should the need arise.

The future of energy supply and energy costs is uncertain. Recent swings in petroleum and natural gas prices serve as timely reminders of our inability to forecast even short-term trends. We now rely on foreign sources for nearly 60% of our petroleum, a greater percentage than in the 1970s. In addition, natural gas imports have increased almost continuously since 1980, and by 1999 accounted for 16% of our natural gas consumption. In contrast to the situation with oil and natural gas, coal is the most stable and abundant fossil energy resource in the United States, and much of the rest of the world. The DOE direct coal liquefaction program represents a prudent investment to mitigate of the risk of future increases in petroleum prices or curtailment of supplies for economic or political reasons.

Acknowledgment. The preprint was derived from Chapter 2 of "Summary Report of the DOE Direct Liquefaction Process Development Campaign of the Late Twentieth Century: Topical Report", Report No. DOE/PC 93054-94, July 2001.

References

- (1) Ashland Synthetic Fuels, Inc. and Airco Energy Company, Inc., *The Breckinridge Project Initial Effort Report VIII*, prepared for U.S. DOE under Cooperative Agreement No. DE-FC05-800R, 1981.
- (2) Bechtel Corporation, *Final Report on Baseline and Improved Baseline Volume VIII, Design, Capital Cost, and Economics For Improved Baseline*, Contract No. DE-AC22-90PC89857, March 1993.
- (3) Hydrocarbon Technologies, Inc., *Direct Liquefaction Proof of Concept Program, DE-92148-TOP-09*, Contract No. DE-AC22-92PC92148, December 1997.

PROGRESS TOWARD THE COAL-FINERY

Harold H. Schobert

The Energy Institute, Penn State University
University Park, PA 16802

Introduction

The conversion of coal to thermal energy or to other fuel forms has usually been considered in the context of a single product. For example, in the direct liquefaction of coal, the goal might be production of the maximum possible liquid yield. An alternative approach is to recognize that there may be valid technical and economic reasons for pursuing a multiple-product strategy, in which coal would be converted to several products—some combination of thermal energy, synthetic fuels, chemical feedstocks, and carbon materials—in a single plant. Such plants have been called coal refineries, coal-fineries, or coalplexes [1]. This paper provides examples of progress, mostly at a laboratory scale, in developing specific experimental findings that can lead to conceptual design of a coal-finery.

Synthetic Liquids, Phenols, or Both

There has been a large effort at Penn State for more than a decade to develop an aviation gas turbine (jet) fuel that would resist pyrolytic decomposition at temperatures to 480°C for up to two hours. One approach to the formulation of such a fuel is to produce a liquid with high concentrations of decalins, to take advantage of the excellent intrinsic pyrolytic stability of these compounds. The increasing dependence of the U.S. on imported petroleum, and the abundance of two-ring structures in some coals, encourage considering producing this fuel from coal.

The direct liquefaction of coal for the specific purpose of making jet fuel was pioneered by Burgess [2,3]. One of her findings was that careful attention must be paid to the structural features present in the coal, primarily elucidated by pyrolysis/ GC/MS and ¹³C NMR, for feedstock characterization [4]. Burgess showed the possibility of producing high yields of two- and three-ring compounds (up to 50% on a dmmf coal basis) provided that the appropriate coal was selected. In her work, the best coal was Pittsburgh No. 8 hvA bituminous. Although a high conversion was achieved, and the liquid was rich in two-ring structures, it also contained significant amounts of phenols, about 10–15% yield. Rather than consider downstream hydrodeoxygenation of the whole product, the phenols were removed by a caustic wash.

If one were to focus only on production of jet fuel, then simultaneous formation of phenols in significant yield could be a detriment to Burgess's process. However, Song and I have argued that significant commercial potential exists for coal-derived phenols [5,6]. Therefore, direct liquefaction of Pittsburgh No. 8 coal at the conditions developed by Burgess (two-stage liquefaction with sulfided molybdenum catalyst and dihydrophenanthrene solvent) could lead to the co-production of a synthetic liquid fuel plus phenols that are not a nuisance, but rather have economic value in their own right.

Subsequently, Kirby investigated the possibility of a “one-pot” liquefaction with simultaneous hydrodeoxygenation [7–11], with bimetallic organometallic compounds as catalyst precursors. It was not intended that such compounds be used on an industrial scale (absent remarkable breakthroughs in their synthesis and handling), but rather sought to explore the potential process benefits from bimetallic dispersed catalysts. Kirby's study included three coals that provided a range of rank (subbituminous B to high-volatile A

bituminous), oxygen content, and, presumably, oxygen functional groups. He showed that the possibility exists to produce high yields of synthetic liquid fuel, *or* high yields of phenols, *or* to co-produce synthetic fuels *and* phenols, provided that the appropriate selection is made of the coal feedstock and the catalyst used [11]. This finding provides significant flexibility in meeting demand for synthetic liquids, for phenols as chemical feedstocks, or both.

Synthetic Liquids and Coke

The intention to produce an advanced thermally stable jet fuel in a commercial-scale demonstration in 2005–2010 has shifted focus away from direct liquefaction, because no liquefaction plants are under construction in the U.S., nor even appear to be in an advanced planning stage. Instead, development now centers on the addition of coal, or coal tar derivatives, to existing refinery infrastructure. Following a suggestion by E.T. Robinson, then of BP Oil, one process being considered is addition of coal to delayed cokers, along with the customary petroleum feed. We have coined the name “co-coking” for this process.

Conceptually, co-coking would provide a liquid product that, on fractionation and hydrotreatment, could be used as synthetic fuel, along with a coke as a co-product. If some of the desirable two-ring structures in the coal would be liberated into the liquid product, hydrotreating would provide a decalin-rich, pyrolytically stable fuel. If, at the same time, the interaction of the coal with the petroleum stream could produce a coke of use for production of carbon materials (i.e., rather than simply a fuel coke), then the by-product credits for the coke could have an impact on the economics of the overall process. In the most favorable scenario, production of a material like needle coke might be the economic “driver” that would more than compensate the expense of producing the jet fuel.

Initial scouting studies by Martin et al. showed the promise of the idea [12,13]. Her work was followed up by Fickinger [14–17] and now by Escallon [18]. A key has been the use of highly fluid coals, particularly to match the temperature of maximum fluidity, or at least most of the plastic range, of the coal with the temperature in the coker. From optical microscopy, it appears that this temperature matching provides the optimum opportunity for coal-petroleum interactions. Yields from co-coking Powellton hvA bituminous coal with FCC decant oil at 465°C were 55–60% total liquids, with distillate boiling in the jet fuel range being 10–12% of the total product yield [17].

It is important to evaluate the prospective uses of the coke, and to assess its potential application beyond use as fuel coke. The most detailed study undertaken so far by Badger et al., studied the possibility of using the “co-coke” as a replacement for petroleum coke in anodes for aluminum smelting [19]. Laboratory-scale test anodes from this “co-coke” exceeded all specifications for anodes, with the sole exception of ash value. Further work on cleaning the parent coals could potentially allow meeting the ash specification as well. Other possible applications of the “co-coke” remain to be investigated, e.g., production of specialty graphites or molded graphite electrodes.

Anthracite

The future for anthracite in traditional combustion applications appears to be bleak. However, there are remarkable opportunities for use of anthracite in the production of premium carbon materials [20]. In part, this is because anthracite already *is* a carbon material, being ≥90% carbon, most or all of which is in large aromatic structures.

Recently, Pappano has shown that anthracite can be graphitized at temperatures ≥2500°C [21]. However, not all anthracites graphitize to the same extent when heat-treated at

identical conditions. Atria has shown that the difference in behavior of anthracites can be related, at least in part, to structural differences [22]. Pappano and his colleagues have shown the possibility of producing a product meeting the specifications of some specialty-grade graphites by replacing the petroleum coke normally used with a selected anthracite [23]. This finding could represent a potential new market for anthracite.

The conventional approach to producing specialty graphites, in addition to using a petroleum coke as the so-called filler, uses coal tar pitch as the binder for the solid particles. The decline of the metallurgical coke industry, and the prospect that there will never be another by-product coke oven battery built in the U.S., calls into question future availability of coal tar pitch. In collateral work, Andréßen studied the possibility of making from anthracite not just a replacement for coal tar pitch, but actually a superior binder [24]. His work has shown that hydrogenation of anthracite at 300°C in the presence of 7 MPa H₂, sulfided molybdenum catalyst, and tetralin yields a pitch of softening point 207°C and atomic H/C ratio of 0.42 [24]. Test specimens of baked carbon bodies have been made successfully with this pitch.

Currently, there are plans to establish a commercial operation for the production of synthesis gas from anthracite in east-central Pennsylvania. The intent is to use the gas to produce low-sulfur, clean diesel fuel via F-T synthesis. However, shifting the synthesis gas to hydrogen would provide the necessary material for mild hydrogenation to produce Andréßen's binder pitch. That pitch, combined with unreacted anthracite, could be used for production of specialty graphite products. Further, Burgess is now conducting a scouting study on the exfoliation of anthracite to make a hydrogen storage medium, by treatment with strong acids followed by thermal shocking [25]. Thus, future vehicular fuel cell applications could use anthracite-derived hydrogen stored on exfoliated anthracite medium, possibly relying also on carbon components of graphitized anthracite and anthracite pitch.

Conclusions

A substantial amount of work over the past decade, albeit mostly at the laboratory scale, has provided data that show the potential for production of multiple products of bituminous and anthracitic ranks. The range of possible products includes distillate fuels (e.g., pyrolytically stable jet fuel), phenols for chemical feedstocks, coke for anode production, binder pitch, graphites, and hydrogen storage media. All of these products are of substantially higher value than the parent coals. Further development of these, and related, processes could establish the opportunity for coal to move aggressively into markets for specialty chemicals and premium carbon materials.

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References

- [1] Grainger, L.; Gibson, J. *Coal Utilisation: Technology, Economics, and Policy*. Graham and Trotman: London, 1981; Chapter 20.
- [2] Burgess, C.E. *Ph.D. Dissertation*. The Pennsylvania State University, University Park, PA, **1994**.
- [3] Burgess, C.E.; Schobert, H.H. *Fuel Proc. Technol.* **2000**, *64*, 57.
- [4] Burgess, C.E.; Schobert, H.H. *Energy Fuels*. **1998**, *12*, 1212.
- [5] Song, C.; Schobert, H.H. *Proc. 16th Intl. Pittsburgh Coal Conf.* **1999**, CD-ROM publication, file 16-4.
- [6] Song, C.; Schobert, H.H. *Energeia*. **2001**, *12(1)*, 1.
- [7] Kirby, S.R.; Song, C.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1995**, *40*, 993.
- [8] Kirby, S.R.; Song, C.; Schobert, H.H. *Proc. 13th Intl. Pittsburgh Coal Conf.* **1996**, 466.
- [9] Kirby, S.R.; Song, C.; Schobert, H.H. *Catal. Today*. **1996**, *31*, 121.
- [10] Kirby, S.R.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1997**, *42*, 643.
- [11] Kirby, S.R. *Ph.D. Dissertation*. The Pennsylvania State University, University Park, PA, **2003**.
- [12] Martin, S.C.; Tomic, J.; Schobert, H.H. *Prepr. Pap. Amer. Chem. Soc. Div. Fuel Chem.* **1997**, *42*, 121.
- [13] Martin, S.C.; Tomic, J.; Schobert, H.H. *Proc. 9th Intl. Conf. Coal Sci.* **1997**, *3*, 1557.
- [14] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1999**, *44*, 106.
- [15] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1999**, *44*, 684.
- [16] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2000**, *45*, 299.
- [17] Fickinger, A.E. *M.S. Thesis*. The Pennsylvania State University, University Park, PA, **2000**.
- [18] Escallon, M.M.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2003**, *48* (in press).
- [19] Badger, M.W.; Mitchell, G.D.; Karacan, O.; Herman, N.; Senger, B.; Adams, A.N.; Schobert, H.H. *US Dept. Energy Rept. No. DE-FC26-98FT40350*, **2001**.
- [20] Andréßen, J.M.; Burgess, C.E.; Pappano, P.J.; Schobert, H.H. *Fuel Proc. Technol.* **2002** (submitted).
- [21] Pappano, P.J. *Ph.D. Dissertation*. The Pennsylvania State University, University Park, PA, **2003**.
- [22] Atria, J.V.; Rusinko, F., Jr.; Schobert, H.H. *Energy Fuels*. **2002**, *16*, (in press).
- [23] Schobert, H.H.; Pappano, P.J. *US Dept. Energy Rept. No. DE-FC26-98FT40350*, **2000**.
- [24] Andréßen, J.M.; Zhang, Y.; Burgess, C.E.; Schobert, H.H. *Fuel Proc. Technol.* **2002** (submitted).
- [25] Burgess, C.E. *Unpublished data*. The Pennsylvania State University, University Park, PA, **2002**.

HTI Coal Conversion Technologies in China

Peizheng Zhou and Theo L.K. Lee
Hydrocarbon Technologies, Inc.
Lawrenceville, New Jersey

Introduction

Hydrocarbon Technologies, Inc. (HTI), its predecessor first founded in 1943 and currently a subsidiary of Headwaters Incorporated, has a long history of developing technologies for converting coal and heavy oil into liquid transportation fuels and chemicals. This presentation describes, in particular, development of HTI coal conversion technologies, including direct coal liquefaction and indirect coal liquefaction, and commercialization efforts of these technologies in China.

Direct Coal Liquefaction (DCL)

Direct coal liquefaction is a technology catalytically converting coal directly into liquid transportation fuels under hydrogen pressure and temperature. HTI has developed under the auspices of U.S. Department of Energy (USDOE), a cost-efficient DCL technology, HTI CoalTM Process. This process operates at a moderate 19 MPa system pressure and 425-450°C reactor temperature and has the following features:

- Two-stage back-mixed (slurry-phase) liquefaction reactors, with relatively simple structure, uniform temperature distribution and ease of temperature control;
- highly active and inexpensive dispersed iron-based catalyst, HTI GelCatTM;
- Optional interstage separator;
- Ashy recycle to enhance catalytic function;
- Fixed-bed Stabilization hydrotreating, either in-line or off-line, to obtain environmentally friendly, very clean liquid fuel products;
- Solvent de-ashing to reject inert materials and coal ash and to recycle heavy organics (de-ashed oil or DAO) to maximize oil yield.

Figure 1 is a schematic of the HTI Coal ProcessTM, showing both in-line and off-line hydrotreating options. Features described above make elevated coal conversion and high oil yield achievable, usually 8-12% higher in distillate yield compared with other direct liquefaction technologies without ashy recycle and DAO recycle. By hydrogenation of coal followed by hydrotreatment of the coal-derived distillate, DCL product has very low sulfur and nitrogen content, and is free of metals and non-distillable resid. These features also yield a good site-specific plant economics, making it economically viable when world oil price is above around \$22-28/bbl.

The U.S. Department of Energy (USDOE) has funded the development of direct coal liquefaction technology since the 1970's oil crisis. In 1996, as part of its Proof-of-Concept Program, the USDOE recommended HTI's direct coal liquefaction technology to the State Science and Technology Commission of China and supported signing of pre-feasibility study and "license in principle" agreements with the Shenhua Group, China's largest coal enterprise, for application of HTI DCL technology. HTI has conducted a

number of bench-scale (25 kg/day) and Process Development Unit (PDU)-scale (3 metric tons/day) tests on various coal samples from Shendong coal field, and a pre-feasibility study including conceptual design. As part of the license-in-principle agreement, HTI provided Shenhua Group with a process design package including four sections: coal liquefaction, GelCat catalyst preparation, solvent de-ashing, and distillate hydrotreating; which constitutes an essential part of the official feasibility study of Shenhua coal direct liquefaction plant. In 2001, with the full support of the U.S. Department of Commerce (USDOC), the U.S. Trade Development Agency (USTDA) funded a technology verification testing. In April 2002, following pilot plant validation, China's State Development Planning Commission completed a comprehensive review of the Shenhua Project.

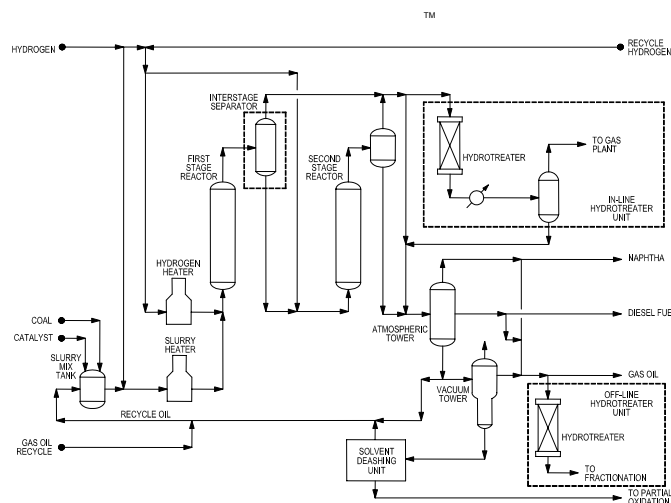


Figure 1. Schematic of HTI Coal Process

Shenhua Group selected the HTI Coal ProcessTM to build the first large-scale commercial coal-to-liquid-fuels plant in the world, after extensive review of processes offered by competing technology providers around the world. On June 18, 2002, HTI signed a process license agreement with Shenhua Group for a direct coal liquefaction plant to be constructed in China, and a signing ceremony was held in Washington, D.C. U.S.A. Under the agreement, HTI will provide the technology license, process design, and technical services. China's State Council approved the official feasibility study of construction of the first direct coal liquefaction plant in China.

The plant will have an ultimate capacity of 50,000 barrels per day of ultra clean, low-sulfur, diesel fuel and gasoline produced from indigenous coal. The license agreement is for three reactor trains planned for the facility, each of which will process approximately 4,300 metric tons of coal per day. Construction of the first reactor train is expected to begin in early 2003 and the plant is expected to start up in 2005. The \$2 billion facility will be located approximately 130 km south of Baotou, at Majiata, Inner Mongolia Autonomous Region of People's Republic of China. In addition to this first facility, Shenhua Group, a 15% owner of the technology, intends to construct three more direct coal liquefaction plants in foreseeable future. Shenhua Group has exhibited foresight in utilizing China's vast coal resources to provide the economy's future energy needs in a highly efficient and environmentally safe manner.

Indirect Coal Liquefaction (Gas-to-Liquids)

Different to direct coal liquefaction, the indirect coal liquefaction (or Gas-to-Liquids) technology first gasifies coal into a mixture of hydrogen and carbon monoxide, called synthesis gas or syngas, which in turn is catalytically converted via Fischer-Tropsch (F-T) reaction into a spectrum of hydrocarbons and oxygenates spanning from methane to waxes. Based on catalyst function and operating conditions, product distribution can be focused on light hydrocarbons, naphtha fraction, or middle distillate, diesel fuels, or heavy products, waxes. One of the most attractive features of F-T synthesis is that its products are extremely clean, free of sulfur, nitrogen, and aromatics; and its diesel fuel product has an remarkably high cetane number, ranging from 76 to 80. Diesel fuels with such a high quality are extremely difficult and costly for refiners to produce from petroleum, if ever possible.

The state-of-the-art F-T technology uses slurry-phase reactors for uniform temperature control and lower reactor cost, however, harsh hydrodynamic conditions in slurry-phase reactors require F-T catalyst to possess high attrition-resistance in addition to high catalytic activity. Prevalent F-T catalysts are either iron- or cobalt-based. Many iron-based F-T catalysts, usually made by co-precipitation method, quickly breaks down into very fine, even sub-micron size particles which are extremely difficult to separate from wax products. This has been a major obstacle for its commercialization. Cobalt-based catalysts are believed to avoid catalyst breakdown and facilitate catalyst/wax separation problems, however, its high cost is hardly justified.

• HTI ZIP Catalyst

HTI has developed a novel iron-based F-T catalyst, HTI ZIP™ catalyst, which is a promoted skeletal iron catalyst. This catalyst does not breakdown as easily as precipitated iron catalysts (Table 1) and is readily separable from waxy F-T products even by simple gravitation sedimentation (Table 2), thus the catalyst/wax separation difficulty is alleviated. HTI ZIP™ catalyst has a high activity comparable to typical precipitated iron catalysts.

Table 1. Catalyst Particle Distribution (wt%)

Particle size (μm)	Fresh catalyst	HTI ZIP (after 500 hours operation in CSTR)	Precipitated iron (after 500 hours operation in CSTR)
44-74	100	25	40
2.5-44	0	70	48
<2.5	0	5	12

Table 2. Catalyst/Wax Separation by Gravity Sedimentation

	HTI ZIP catalyst	Precipitated iron catalyst
Catalyst in slurry, wt%	15	3.0
Settling temperature, °C	Solids concentration after settling (wt%) and efficiency (%)	
130	0.132 (99.1)	1.372 (54.3)
185	0.085 (99.4)	0.938 (68.7)
205	0.069 (99.5)	0.882 (70.7)

• HTI Slurry-Phase GTL Process

On the basis of the unique properties of HTI ZIP catalyst, a HTI Gas-to-Liquids (GTL) Process has been developed, which employs simple gravity settling for catalyst/wax separation (Figure 2). HTI just completed a feasibility study using HTI ZIP catalyst and slurry-phase GTL process for a Chinese client to convert natural gas-derived syngas to produce petrochemicals.

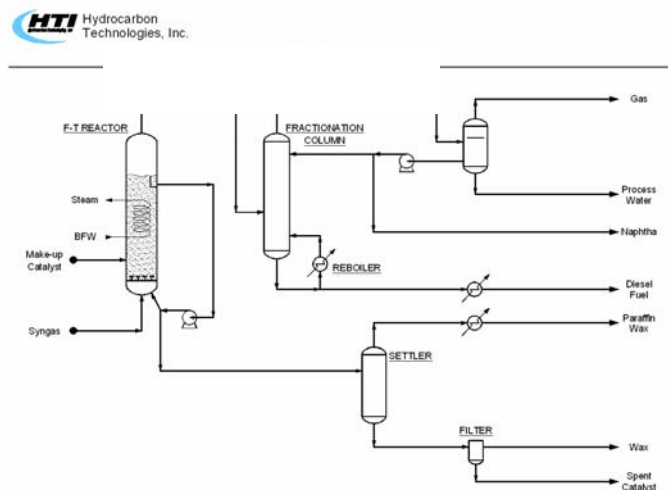


Figure 2. Schematic of HTI Slurry-Phase GTL Process

• HTI Integrated Fuel-Ammonia Co-Production Process

As a new development of HTI GTL technology, HTI has coined an innovative concept of integrating ammonia production with F-T synthesis, thus developed HTI Integrated Fuels-Ammonia Co-Production Process. This process was designed for small-size and medium-size, coal-based in particular, ammonia synthesis plants in countries such as China where imported ammonia fertilizers are threatening survival of local fertilizer producers. By retrofitting existing small- and medium-sized ammonia plants via addition of a GTL unit between syngas manufacture and ammonia synthesis, most of carbon monoxide and a portion of hydrogen in syngas are first converted to hydrocarbon fuels, while remaining hydrogen is further utilized to produce ammonia. Doing so, product slate of these plants is greatly changed to produce high-valued ultra clean diesel fuels and naphtha as major products, which have a broad market, while ammonia production is substantially reduced. Furthermore, the product slate (proportion of fuels and ammonia production) can be adjusted according to seasonal demand, thus providing significant flexibility in plant operation. Plant economics is thus dramatically improved. Preliminary assessment was conducted for eleven (11) small- and medium-sized ammonia plants, and results are very encouraging. Currently we are conducting a feasibility study for a Chinese chemical company to retrofit a small ammonia plant. This process is graphically demonstrated in Figure 3.

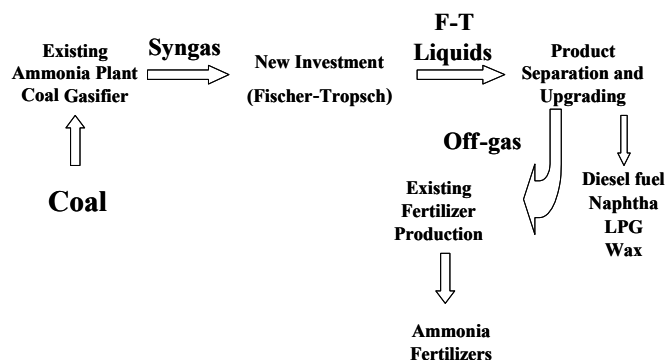


Figure 3. HTI Integrated Fuels-Ammonia Co-Production Process

Concluding Remarks

HTI has successfully developed a direct coal liquefaction technology which is co-owned by Shenhua Group and is currently being applied to the first large-scale commercial direct coal liquefaction plant. HTI is grateful to USDOE, USDOC, and USTDA for their strong support. HTI also developed promoted skeletal iron catalyst that is easy to separate from waxy F-T products, a Slurry-Phase GTL Process based on skeletal iron catalyst, and Integrated Fuels-Ammonia Co-Production Process which is believed to be very useful for retrofitting small- and medium-sized ammonia plants.

COAL-BASED JET FUEL: COMPOSITION, THERMAL STABILITY AND PROPERTIES

Suchada Butnark¹, Mark W. Badger¹,
Harold H. Schobert¹ and Geoffrey R. Wilson²

¹The Energy Institute, The Pennsylvania State University,
C211 Coal Utilization Lab, University Park, PA 16802

²PARC Technical Services, 100 William Pitt Way, Pittsburgh,
PA 15238

Introduction

The future use of jet fuel as a primary coolant for on-board heat sources of high-performance jet aircraft flying at high speeds will have an increased thermal stability requirement [1-3]. Currently, the conventional jet fuel for military aircraft, JP-8, is produced from petroleum through well-known refinery processes. However, it has been shown to be less stable in the pyrolytic regime than a coal-derived jet fuel [1]. Unlike long-chain alkanes in petroleum-derived jet fuel such as JP-8, the cyclic structures, such as cycloalkanes and hydroaromatics, in coal-derived material have shown significant improvement of thermal stability and high energy density. Thus, the coal-derived materials can be incrementally incorporated into existing refinery operation for thermally stable coal-based jet fuel production. The fuel, the so-called JP-900, is expected to not decompose when operating at pyrolytic temperatures as high as 900°F (482°C).

In addition to the thermal stability improvement, the alternative jet fuel production has been developed due to the availability of potential coal resources as a strategic hedge against possible curtailment of petroleum imports. The pilot-scale production of prototype JP-900 has been performed on a petroleum refinery stream (light cycle oil (LCO)) and a coal-derived liquid (refined chemical oil (RCO)) described elsewhere [4]. In the present work, the candidate products from the hydrotreatment and dearomatization processes were studied to obtain the optimum composition that provides prototype JP-900 a highest thermal stability and appropriate physical properties.

Experimental

Samples.

The pilot-scale production of six jet fuel samples used in this work was done by PARC Technical Services, Harmaville, PA. The LCO, RCO and their 1:1 blend underwent severe hydrotreatment in order to achieve an extremely low heteroatom content, thus avoiding the poisoning of the noble metal catalyst used in the aromatic saturation step [4]. Crosfield NiMo catalyst was used for hydrotreatment of LCO, RCO and their 1:1 blend using at 710 psi and 685-725°C [4, 5]. The hydrotreated products are called HDT LCO, HDT RCO and HDT (LCO/RCO).

The aromatic saturation was performed on each of the hydrotreated samples under 2100 psi and 400-500°C, using Engelhard Pt-Pd catalyst [4, 5]. These saturated fuels are called SAT LCO, SAT RCO and SAT (LCO/RCO).

Characterization.

Jet fuel candidates was characterized using a Shimadzu GC-17 coupled with Shimadzu QP-5000 MS detector fitted with a Restek XTi-5 column with dimension of 30 m, 0.25 mmID and 0.25 µm df (5% phenyl film thickness). Nine basic compound classes were determined as:

Class 1: alkane

Class 2: alkene, alkyne, and cyclo-alkene

Class 3: cycloalkane

Class 4: hydroaromatic

Class 5: alkylbenzene

Class 6: naphthalene and methylnaphthalene

Class 7: other aromatics (biphenyl and 3-, 4-ring aromatics)

Class 8: decalin and methyldecalin

Class 9: tetralin and methyltetralin

For a quantitative GC analysis, tetrahydrofuran, an internal standard, was used to quantify the weight percentage from GC intensity of nine classes' major compounds.

Thermal Stability in Batch Conditions (Static Test).

The thermal stability tests of JP-900 fuel candidates have been studied in various flow systems in autoxidative and pyrolytic regimes [6, 7]. In this work, the static tests in batch reactors have been performed in the pyrolytic regime at very high temperatures in the absence of oxygen [8]. Pyrolytic stability was determined by heating 5 ml of sample in a 25 ml microautoclave at 480°C under 100 psig of UHP N₂ for 5, 15, 30, 45, 60, 120, 180 and 240 minutes. After completion each pyrolysis run, the micro- autoclave was cooled and the weight percent of the solids, liquids and gases produced was determined. The method is described elsewhere [1, 9] and the error in the measurements is about ± 0.1 wt% [10]. The liquid products were also analyzed by GC/MS.

Physical Properties Testing.

Net heat of combustion, an indication of combustion performance, was measured using a Parr Calorimeter (Model 1563) followed ASTM D 2015. The error associated with the measured value was ± 60 BTU/lb.

Flash point in this study was measured using a continuously closed cup flash point tester (MINIFLASH-FLP from Grabner Instruments), which used 1-mL sample with no open flame and 30-second manipulation time. The repeatability was ± 2°F.

The measurement of Saybolt universal viscosity was performed at 100°F in Saybolt universal seconds (SUS). The conversion of Saybolt universal viscosity to kinematic viscosity in centistokes (cSt) followed the ASTM D 2161.

Smoke point is the minimum flame height at which soot comes from a laminar diffusion flame tip generated by a standard wick burner. It was measured under ASTM D 1322 and could predict the soot formation tendency of aviation gas turbine fuels. The repeatability of the test was 2 mm.

Results and Discussion

Chemical Composition of Samples.

Table 1 displays the nine compound classes taken from the conventional JP-8 and six prototype JP-900 fuels. Unlike JP-8, all six fuel candidates have more cyclic structures than long-chain components. The hydrotreated fuels (HDT LCO, HDT (LCO/RCO) and HDT RCO) show a greater distribution of components in different classes and have higher aromatic and tetralin contents. Upon saturation, the major components for saturated fuels (SAT LCO, SAT (LCO/RCO) and SAT RCO) were converted to cycloalkanes, primarily decalin. Decalin and tetralin are preferred components for prototype JP-900 [11-13]; however, it is also important to take the other properties into consideration.

Table 1. The Overall Composition (in weight%) of Conventional JP-8, Hydrotreated and Saturated Fuels.

Fuel	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6	Class 7	Class 8	Class 9
JP-8	72.11	5.65	9.80	0.63	7.92	2.27	1.16	0.00	0.46
HDT LCO	15.30	8.03	2.85	2.71	27.52	11.00	0.41	11.24	20.94
HDT (LCO/RCO)	6.66	0.55	2.54	7.35	10.97	12.06	12.13	11.56	36.17
HDT RCO	0.50	0.00	2.30	7.33	3.77	16.93	17.68	13.13	38.37
SAT LCO	14.61	21.01	19.92	0.00	0.58	1.94	0.00	35.21	6.73
SAT (LCO/RCO)	6.24	7.44	21.92	0.00	0.15	0.00	0.00	61.66	2.58
SAT RCO	3.13	3.07	19.73	0.00	0.04	0.00	0.00	74.04	0.00

Thermal Stability in Batch System.

After thermal stressing of hydrotreated and saturated fuels in pyrolytic regime at different resident times, the solid deposits and gas formed were collected, presented in term of remaining liquids (stressed fuels) in Figure 1.

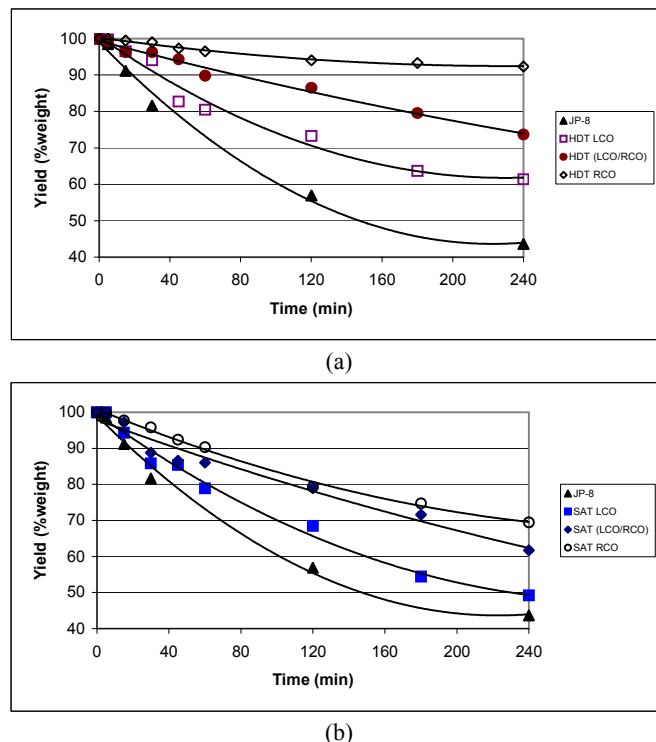


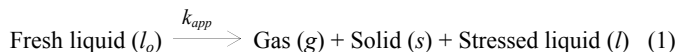
Figure 1. Remaining liquid after being stressed at 480°C compared to JP-8: (a) hydrotreated fuels and (b) saturated fuels.

A Simple Kinetic Model.

To study the jet fuel reaction in batch system, simple kinetic models of similar hydrocarbon mixture have been previously discussed [14, 15]. However, it is still impractical to model the chemical changes of all components of a real mixture like jet fuel that is comprised of hundreds of chemical species [16]. For six jet fuel candidates, a simple model is proposed to describe the time dependence of the liquid degradation to gas, solid and remaining

stressed liquid (Equation 1). The stressing at 480°C in batch system at long resident time can represent the most severe thermal stressing that the fuels can experience.

Liquid degradation:



The initial concentration (weight) of fresh liquid is denoted by C_{l_o} whereas the amount remaining after a particular thermal-stressing time (t) at 480°C is expressed by C_l . Assuming an apparent first-order equation, the rate of liquid degradation (r_l) can be written in the form:

$$r_l = -dC_l/dt = k_{app}C_l \quad (2)$$

Therefore;

$$\begin{aligned} C_l &= C_{l_o} \exp(-k_{app}t) \\ \ln [C_l/C_{l_o}] &= -k_{app}t \end{aligned} \quad (3)$$

The plot of $\ln [C_l/C_{l_o}]$ vs t gives a slope $-k_{app}$ (an apparent rate constant). Figure 2(a) and 2(b) show that the degradation rate of JP-8, hydrotreated and saturated fuels behave good fittings with a first-order model. Thus, the apparent degradation rate constant can be quantitatively expressed in the trends of thermal stability for all fuels. As displayed in Table 2, both fuel candidates, especially HDT (LCO/RCO) and HDT RCO, have shown lower apparent rate constants than that of JP-8. Especially, the HDT RCO, dominated by its tetralin component, has exhibited the lowest thermal degradation. Considering the apparent degradation rate constants, all jet fuel candidates are more stable than the JP-8.

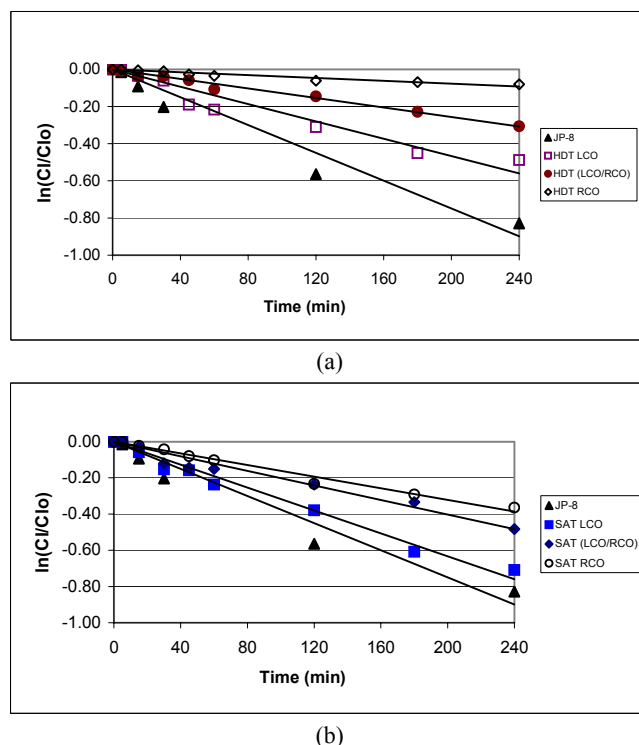


Figure 2. Plot of $\ln [C_l/C_{l_o}]$ vs t for (a) hydrotreated fuels and (b) saturated fuels at 480°C and compared to JP-8.

From general observation, the increasing concentration of refined chemical oil (RCO) to the feedstock blends of both hydrotreated and saturated fuels yielded lower solid deposition and

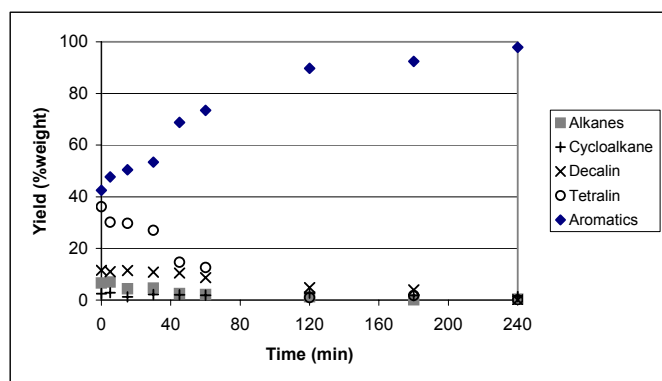
gas formation (inhibited degradation of liquid). This may be due to a high aromatic content, presence of a hydrogen donor such as tetralin, and the low alkane concentration.

Table 2. k_{app} for Fuel Candidates Obtained from Figure 2.

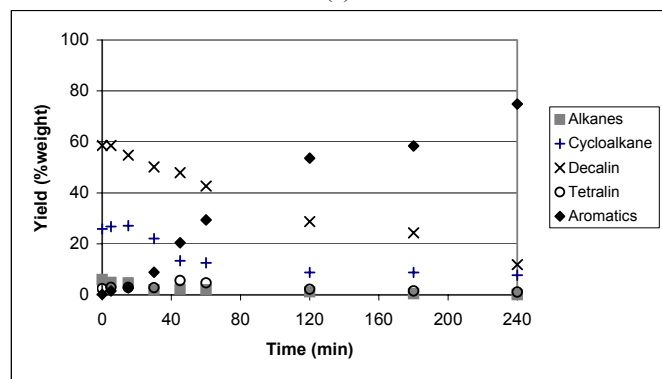
Fuel	$-k_{app} \text{ (min}^{-1}\text{)}$
JP-8	0.0040
HDT LCO	0.0023
HDT (LCO/RCO)	0.0013
HDT RCO	0.0004
SAT LCO	0.0032
SAT (LCO/RCO)	0.0020
SAT RCO	0.0016

Overall Chemical Changes during Stressing.

Examples of product distribution of a hydrotreated fuel and a saturated fuel have been determined from GC/MS. Figure 3(a) and 3(b) display the chemical changes during stressing HDT (LCO/RCO) and SAT (LCO/RCO) respectively.



(a)



(b)

Figure 3. Distribution of chemical composition for fresh fuels and their liquid products after stressing at 480°C: (a) HDT (LCO/RCO), and (b) SAT (LCO/RCO).

For stressed HDT (LCO/RCO), the increase in aromatic content was significant, starting from 45 to 240 minutes. Tetralin, a hydrogen donor in hydrotreated fuels, was substantially decreased after the 45-minute reaction. After this time period, the small amounts of alkanes, cycloalkanes and decalin were all converted to aromatic to almost 100% at 240 minutes. Most of converted aromatics (not shown here) are mainly 3- and 4- ring aromatics, followed by naphthalene and alkylbenzenes.

Compared to HDT (LCO/RCO), SAT (LCO/RCO) is mostly comprised of thermally stable compounds such as decalin and cycloalkanes. However, these components were significantly converted to aromatics after 45 minutes, as well as those of HDT (LCO/RCO). Tetralin slightly rose from 5 to 45 minutes and dehydrogenated to naphthalene after 60 minutes. The major aromatic contents for SAT (LCO/RCO) as increase of resident time are naphthalene and alkylbenzenes.

Physical Properties.

Table 2 shows the physical properties of all fuels. The heat of combustion values of six JP-900 fuels do not differ greatly from that of JP-8 despite differences in chemical composition. The hydrotreated fuels appear to be low in net heat of combustion due to highly aromatic and low alkane concentration. However, with the presence of aromatic content, the fuels' density and energy density are significantly high. A heavy fuel of high energy density is desirable when storage volume limits fuel capacity [17].

The other problem associated with high aromatic contents is low smoke point, resulting in high sooting tendencies and emissions [18] as seen from tests with the hydrotreated fuels. The specification for minimum smoke point, 19 mm [19, 20], is achieved only by the saturated fuels.

For other properties, all coal-based jet fuels' flash points and viscosities meet the ASTM D 1655 specification (MIN. 100°F and MAX 8.0 cst at -20°C, respectively) [20].

To this point, the most important factor for a new formula of JP-900 would be aromatic contents, including tetralin that helps improve thermal stability in pyrolytic regime but tends to give low smoke point. The current aromatics in conventional jet fuel are about 25 volume% [19, 20]. However, the specification for future jet fuel may have to increase aromatic contents [21] to improve the fuel's thermal stability and energy density.

Table 3. The Physical Properties of JP-8, Hydrotreated and Saturated Fuels.

Fuel	Heat of combustion (BTU/lb)	Density (kg/L)	Energy density (MJ/L)	Flash point (°F)	Viscosity (cSt)	Smoke point (mm)
JP-8	19880	0.81	37.42	124.1	1.7	23.6
HDT LCO	19140	0.89	39.53	171.1	2.4	8.2
HDT (LCO/RCO)	18750	0.93	40.55	163.0	2.6	6.5
HDT RCO	18260	0.97	41.33	157.1	2.0	5.8
SAT LCO	19886	0.84	38.36	148.0	2.7	24.1
SAT (LCO/RCO)	19500	0.86	39.13	145.0	2.7	22.8
SAT RCO	19440	0.88	39.55	139.1	2.8	19.6

Conclusions

Coal-based jet fuels from hydrotreatment and saturation of light cycle oil and refine chemical oil have shown a great improvement of thermal stability in the pyrolytic regime in batch system. The fuel's physical properties, such as energy density, flash point and viscosity, have also shown encouraging results. However, the main concern of JP-900 is the excess of aromatic content in hydrotreated fuels, resulting in low smoke points or poor combustion performance. To establish the right formula for JP-900, the compromise must be made

on thermal stability, physical properties and distribution of compound classes.

Acknowledgement.

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References

1. Song, C., Eser, S., Schobert, H.H. and Hatcher, P.G., *Energy & Fuels*, 1993. **7**: p. 234-243.
2. Heneghan, S.P., Zabarnick, S., Ballal, D.R. and Harrison III, W.E., *Journal of Energy Resources Technology*, 1996. **118**: p. 170-179.
3. Edwards, T., AIAA 93-0807, *31st Aerospace Sciences Meeting and Exhibit*, Reno, Nevada, 1993: p. 1-11.
4. Wilson, G.R., *Project Report on AFOSR-Subcontract for Advanced Thermally Stable Coal-Based Jet Fuels for the Pennsylvania State University*. May 2000, PARC Technical Services Inc. (Pittsburgh, PA) to Pennsylvania State University.
5. Badger, M.W., *Preprints of Papers, American Chemical Society Division of Petroleum Chemistry*, 2000. **45**(3): p. 531-533.
6. Roan, M.A. and Boehman, A.L., *Preprints of Papers, American Chemical Society Division of Petroleum Chemistry*, 2002.
7. Andrésen, J.M., Strohm, J.J., Boyer, M.L., Song, C., Schobert, H.H. and Butnark, S., *Preprints of Papers, American Chemical Society Division of Fuel Chemistry*, 2001. **46**(1): p. 208-210.
8. Hazlett, R.N., *Thermal Oxidation Stability of Aviation Turbine Fuels (Monograph: 1)*, ASTM 1991, Philadelphia, PA.
9. Strohm, J.J., Andrésen, J. M. and Song, C., *Preprints of Papers, American Chemical Society Division of Petroleum Chemistry*, 1999. **44**(3): p. 386-390.
10. Andrésen, J.M., Strohm, J.J., Sun, L. and Song, C., *Energy & Fuels*, 2001. **15**(3): p. 714-723.
11. Butnark, S., Badger, M. and Schobert, H.H., *Preprints of Papers, American Chemical Society Division of Fuel Chemistry*, 2001. **46**(2): p. 492-494.
12. Butnark, S., Badger, M. and Schobert, H.H., *Preprints of Papers, American Chemical Society Division of Fuel Chemistry*, 1999. **44**(3).
13. Butnark, S., Master Thesis 1999, The Pennsylvania State University.
14. Yoon, E.M., Selvaraj, L., Eser, S. and Coleman, M.M., *Energy & Fuels*, 1996. **10**: p. 812-815.
15. Veytsman, B. and Coleman, M.M. *Preprints of Papers, American Chemical Society Division of Petroleum Chemistry*. 1998.
16. Zabarnick, S., *Energy & Fuels*, 1998. **12**: p. 547-553.
17. Goodger, E.a.V., R., *Aviation Fuels Technology*. 1985, Hong Kong: MacMillan Publishers Ltd.
18. Pande, G.S. and Hardy, D.R., *Energy & Fuels*, 1995. **9**: p. 448-457.
19. Coordinating Research Council, *Handbook of Aviation Fuel Properties, Society of Automotive Engineers, CRC Report No. 530*. 1983.
20. ASTM, *Annual book of ASTM standards*. 2000: Philadelphia, PA.
21. Kirklin, P.W. and David, P., *Aviation Fuel: Thermal Stability Requirements*. 1992, Philadelphia, PA: ASTM.

INVESTIGATION OF CO ADSORPTION ON THE ZIRCONIA POLYMORPHS

Zhongyi Ma, RunXu, Cheng Yang, Wei Wei, Yuhua Sun

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, P.R.China 030001

Introduction

In recent years, interest has grown in the surface properties of microcrystalline zirconia, in view of its wide use as a catalyst, metal catalyst support, and precursor for ceramic applications. The most used probe molecule for testing the chemical properties of oxides in particular of zirconia, is CO. Different zirconia phase have great difference in adsorption CO because of different surface chemical properties. In this present the interactions of CO with amorphous, monoclinic and tetragonal zirconia are investigated by both infrared spectroscopy and temperature-programmed spectroscopy to determine the influence of bulk phase on adsorption capacity and species formed by CO reaction with hydroxyl on zirconia surface.

Results and discussion

Figure1 showed that the infrared spectra of CO adsorption on the am-ZrO₂ with temperature increasing. Below 523 K, obvious spectra could not be seen. With temperature increasing, CO adsorption bands at 2132cm⁻¹ could be detected. The bands at 1558cm⁻¹ and 1369cm⁻¹ are considered to the formate bands, which could be proved with bands at 2973cm⁻¹ and 2888cm⁻¹ for CH (not show). There were different from what W.Hertl^[1] observed in which formate was not detected while carbonate formed. Figure 4 showed that TPD spectra of am-ZrO₂ adsorption of CO at temperatures at 673K. Three species desorbing in this case were CO, CO₂ and H₂O, which could attribute to the thermal decomposition of formate and desorption of adsorption CO.

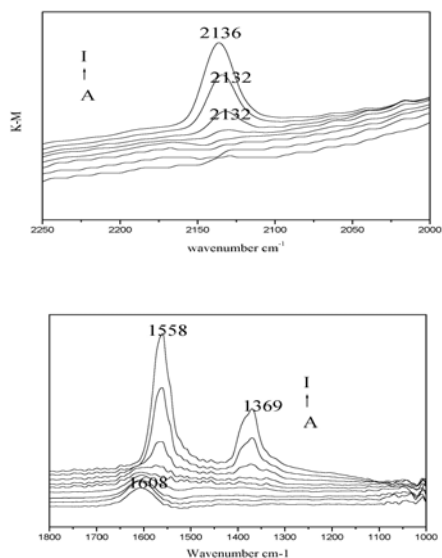


Figure1. Spectra of CO adsorption on am-ZrO₂. A-303K, B-323K, C-373K, D-I-423-673K

CO adsorption spectra on the m-ZrO₂ with temperature increasing were showed in Figure2. Two weak bands at 2121cm⁻¹ and 2105cm⁻¹ were detected at 473K, when temperature increased, two bands merge and only one band at 2109 was seen. At low temperature

bidentate bicarbonate with bands at 1631cm⁻¹ and 1481cm⁻¹ were observed while formate bands at 1573cm⁻¹, 1384cm⁻¹ and 1361cm⁻¹ formed when temperature increased up to 576K, which were similar to what Konstantin Pokrovski reported^[2]. TPD-MS species were same to the am-ZrO₂ and only three species could be detected. But three CO₂ peaks were showed and CO desorption temperature was lower than that of am-ZrO₂. IR spectra showed that the bicarbonate and formate species formed when CO adsorption on m-ZrO₂, with temperature increasing, these species were decomposed.

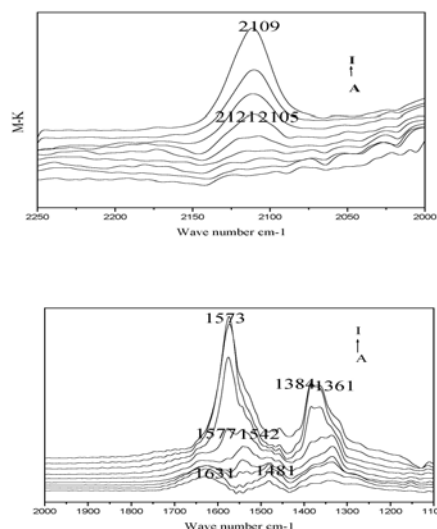


Figure2. Spectra of CO adsorption on m-ZrO₂. A-303K, B-323K, C-373K, D-I-423-673K

IR spectra of CO adsorption on the t-ZrO₂ were showed in Figure3. Below 573K obvious bands could hardly be seen. When temperature increased, two bands in 2183cm⁻¹ and 2090cm⁻¹ were detected, which differ from what detected on the am-ZrO₂ and m-ZrO₂. When temperature was below 623K, bidentate carbonate with bands in 1658cm⁻¹ and 1288cm⁻¹ were obvious, bidentate bicarbonate with bands in 1612 cm⁻¹ and 1357cm⁻¹ were formed when temperature up to 623K. But polydentate reported by Konstantin Pokrovski^[2] could hardly be detected. CO-TPD-MS (Figure4) showed that the different species were desorbed when CO adsorption at 623K, besides H₂O CO and CO₂, H₂ was desorbed. We could speculate that there were different chemical properties in the zirconia polymorphs.

In addition, the concentration and basicity of hydroxyl groups were different on the zirconia polymorphs and as well as Lewis acidity of Zr⁴⁺ cation and Lewis basicity of O²⁻, which exerted great influence on CO adsorption and species formed on different zirconia phase when CO reacted with hydroxyl on zirconia polymorphs. The detail mechanism was under investigation.

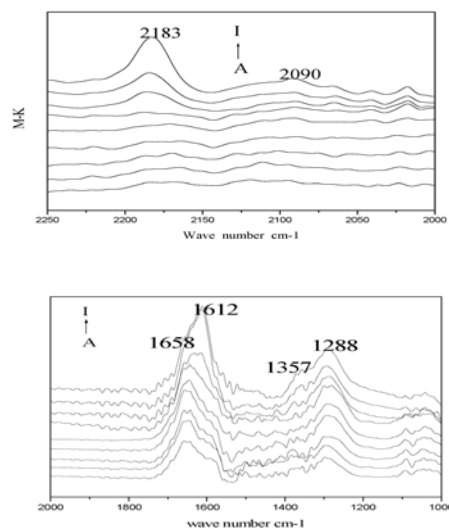


Figure3. Spectra of CO adsorption on t-ZrO₂. A-303K, B-323K, C-373K, D-I-423-673K

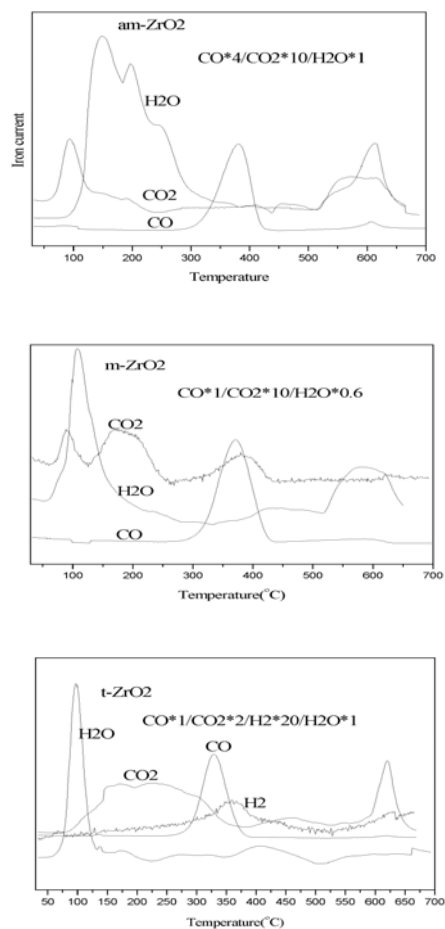


Figure 4 CO-TPD-MS spectra of am-ZrO₂, m-ZrO₂ and t-ZrO₂. Adsorption CO at 623K

Reference:

- (1) W. Hertl *Langmuir* **1989**, 5(1), 96-100.
- (2) Konstantin Pokrovski, Kyeong Taek Jung, and Alexis T. Bell, *Langmuir*.**2001**,17 (14) 4297-4303

REMOVAL OF HETEROATOM CONTAINING SPECIES IN COAL LIQUID DISTILLATES FROM SOUTH BANKO COAL BY CATALYTIC HYDROTREATMENT OVER NiMo SUPPORTED ALUMINA CATALYST

SRI DJANGKUNG SUMBOGO MURTI¹⁾, KINYA SAKANISHI²⁾, OSAMU OKUMA³⁾, YOZO KORAI¹⁾ and ISAO MOCHIDA¹⁾*

1. Institute of Advanced material Study, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
2. National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan and
3. The New Industry Research Organization, 1-5-2, Minatojima-minamimachi, Chuo-ku, kobe 650-0047, Japan

INTRODUCTION

Coal liquid distillates ranging in the boiling point from naphtha to gas oil fractions tends to contain more heteroatoms such as nitrogen and oxygen than the corresponding petroleum product [1]. Removal of these heteroatom is required before using as feedstock for existing refineries, because these elements are sources of air pollution and causes for severe deactivation catalysts.

Heteroatom, S, N and O, in aromatic rings required sulfided NiMo, CoMo or NiW catalysts for their extensive removal to required levels in petroleum refining. Sulfur is eliminated directly by the catalyst to form H₂S, although sterically hindered S compounds are hardly removed unless the hydrogenation of neighboring aromatic ring releases the hindrance [2]. In contrast, denitrogenation and deoxygenation required complete hydrogenation of aromatic rings because of strong C-N and C-O bonds [3]

In the present study, hydrotreatment of South Banko coal liquids was carried out over commercially available NiMo/Al₂O₃ catalysts. The effect of reaction conditions such temperature, contact time and amount of catalyst on heteroatom removal was studied. HDS, HDN and HDO reactivities of some heteroatoms containing species were also investigated.

EXPERIMENTAL

I. Feedstocks.

Coal liquid used in the present study was obtained from coal liquefaction pilot plant in Japan. The boiling range of the sample is < 300 °C, and contained 0.84wt% of N, 3.74wt% of O and 900ppm S.

II. Hydrotreatment

The coal liquid was hydrotreated over a commercial NiMo/Al₂O₃ catalysts in autoclave-type reactor (100 ml internal volume). 10 g oil, 1 g catalyst, which was pre-sulfided by 5%H₂S/H₂ at 360°C for 2 hours, and 10 kg/cm² hydrogen gas were charged into the reactor. The reactor was heated to prescribed temperature and maintained for 2h. The hydrotreated product was filter and analyzed by GC-AED to qualify and quantify all the heteroatom containing compounds.

RESULTS AND DISCUSSION

Fig. 1 showed carbon, sulfur, nitrogen and oxygen chromatograms feed analyzed by GC-AED. Most of sulfur species in SBCL were thiophenes (TH) and benzothiophenes (BT). Pyridines, aniline quinolines, and indoles were found as nitrogen, phenols, benzofurans and dibenzofuran were as oxygen compounds. Hump on the nitrogen chromatogram due to nitrogen species was observed in this feed, indicating basic nitrogen species in the SBCL.

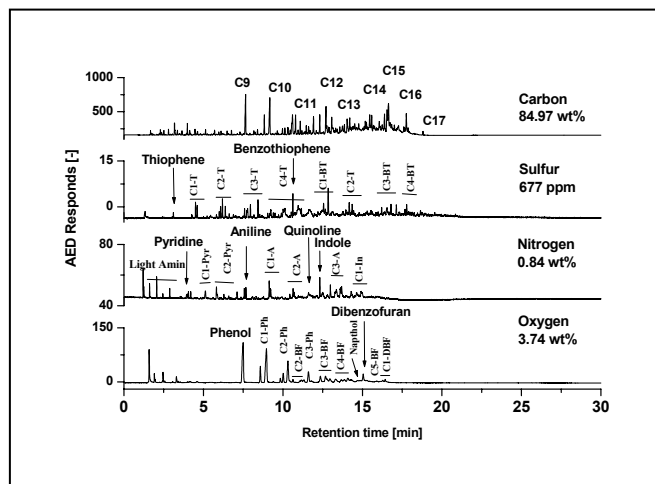


Figure 1. GC-AED chromatograms of SBCL.

The reactivity of sulfur species after hydrotreatment over NiMo/Al₂O₃ catalysts are shown in Figure 2. All sulfur species found in SBCL showed the high reactivity over the NiMo catalyst, and removed by 360 °C for 60 min.

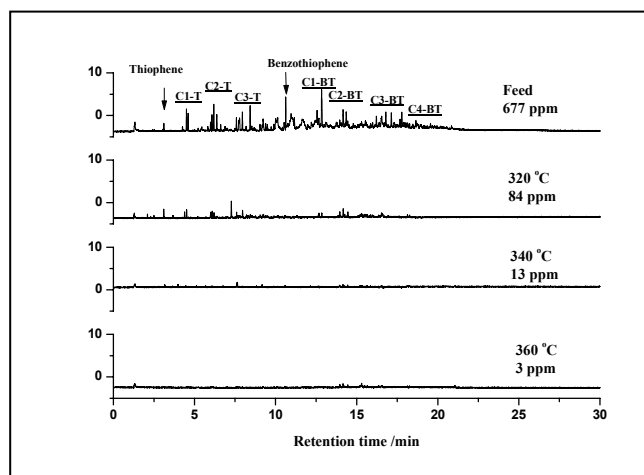


Figure 2. Sulfur chromatogram of hydrotreated SBCL.

In contrast, nitrogen species exhibited a wide range of reactivity. Pyridines exhibited high reactivity, however, anilines and quinoline were much less reactive. Nitrogen conversion after HDN is listed in Table 1. The surprising result of this study is that at high HDN conversions the majority of the compounds remaining in the hydrotreated products are alkylated anilines. Thus, alkylated anilines are the compounds most difficult to convert from coal liquid. At a higher temperature of 400 °C, alkylated anilines were as the lowest reactivity, lower even than quinolines. It is surprising since anilines has an aliphatic C-N bond whereas quinolines have the nitrogen atom included in the six-membered ring structure. Another study has noted that 3-ethyl aniline showed a lower reactivity than quinoline when both were present in the reaction mixture while it showed a higher reactivity than quinoline when reacted alone.

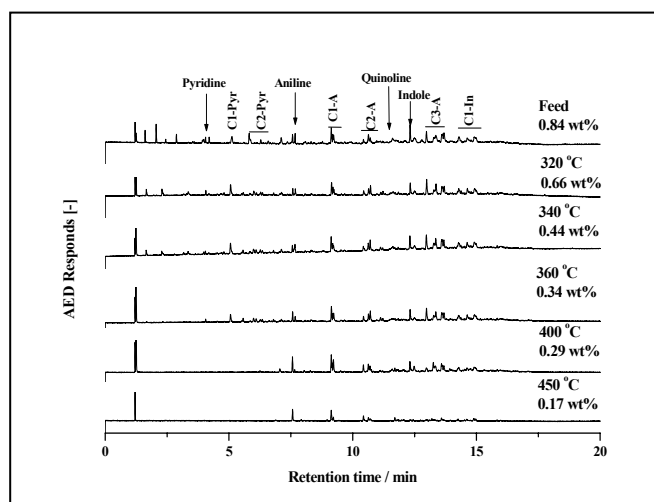


Figure 3. Nitrogen chromatograms of hydrotreated SBCL.

Table 1. Nitrogen species conversion (ppm).

	Feed	320	340	360	400	450
Light Amin	547	368	256	232	336	176
Pyridine	143	185	50	0	0	0
c1-Pyr	310	334	261	173	0	0
c2-Pyr	587	399	301	225	45	0
Aniline	155	136	101	151	239	197
c1-A	629	444	432	293	366	284
c2-A	951	746	545	506	588	334
c3-A	2606	2014	1302	1070	888	387
Quinoline	322	244	141	120	115	88
Indole	427	342	210	184	179	48
c1-In	1385	1118	506	448	391	319
Un-known	884	686	569	185	40	28
Total	8418	6649	4418	3356	2851	1687

Oxygen species, 3.74 wt% of feed, exhibited low reactivity over NiMo catalyst especially dibenzofuran as showed in Figure 4.

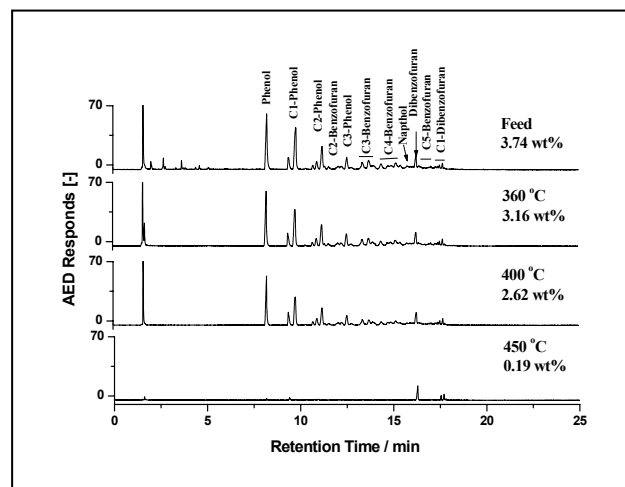


Figure 4. Oxygen chromatograms of hydrotreated SBCL.

References

1. Yanai, S., Komatsu, N., Shimasaki, K., *proceedins the 6th Japan China Symposium on Coal and C1 Chemistry*, Miyagi, Japan (1998) 196
2. Ma, X., Sakanishi, K., Mochida, I., *Ind. Eng. Chem. Res.* **33** (1994) 218
3. Girgis, M.J., Gates, B.C., *Ind. Eng. Chem. Res.* **30** (1991) 2021.

STUDY OF THE LIQUIDS DERIVED FROM CO-COKING IN A LABORATORY SCALE DELAYED COKER

María M. Escallón, Gareth Mitchell, Harold H. Schobert and Mark W. Badger

The Energy Institute, the Pennsylvania State University,
PA 16802

KEYWORDS: Co-coking, Jet Fuel, Gasoline

Introduction

Co-coking is the simultaneous coking of a bituminous coal and petroleum product, such as decant oil. The advantage of co-coking relative to the better-known co-processing is that co-coking can be carried out at relatively low-pressures and that hydrogen is not required in the process [1]. Delayed coking of petroleum streams has been widely used for the conversion of heavy distillates into lighter ones. By the use of an appropriate aromatic feedstock, in addition to the conversion into lighter distillates, this process produces needle coke. Extensive work at our Institute has shown that the inclusion of coal-derived components brings more pyrolytic stability to the distillates [2-6].

Many studies have been performed in order to improve the quality of the jet fuel by blending coal and petroleum [7-20]. It has been seen that these blends give to the distillates thermal stability because of the production of hydroaromatic or naphthenic compounds. This is desirable for the jet fuel to reduce formation of deposits that can lead to the obstruction of the aircraft's fuel lines or burner nozzles.

For the future characterization, S.A.R.A analysis (saturates, aromatics, resins, asphaltenes) will be carried out to determine the contribution of the coal to the final liquid yield with respect to reaction time in co-coking. The components of each fraction will be identified by mass spectrometry. A blank of decant oil (100%) at 6 h was run in order to compare the contribution of the coal to the final liquid yield.

Experimental

The experimental procedure has been described in a companion preprint in this volume. The reactor has three sections, bomb, transfer pipe and catchpot. Approximately 20 g of the mixture decant oil / coal (2:1) was added to the bomb of the reactor. A blank with 20g of pure decant oil was run at six hours to compare the coke obtained with those of co-coking.

The reactor is assembled and purged with N₂. The reactor is heated in a sand bath at a constant temperature of 465°C, varying the reaction time from 2 up to 12 hours. When the reaction at each specific temperature has finished, the reactor is allowed to cool at room temperature. After reaching this temperature, the three sections are disconnected.

The solid product which is in the bomb goes through Soxhlet extraction with THF and the insoluble material is dried for 1 hour at 100°C in an oven. The weight of the coke before and after the extraction was recorded to get the amount of THF-solubles in the coke. For the mass balance, the THF-solubles were added to the liquid yield.

The characterization of jet the liquid was carried out using a Hewlett Packard 5800 GC with flame ionization detector. Simulated distillation, following ASTM D2887. This is useful to explore boiling point distributions in complex mixtures, usually fuel related.

Samples. Decant oil: Obtained from Seadrift Coke in Texas. This feed is used for making premium needle coke.

Coal: A number of compatible coals with regard to thermoplastic properties, ash and sulfur values were evaluated in past investigations [1,7-10,12,13,18]; this work has led to the selection of Powellton coal as a feedstock of choice. This coal was obtained previously cleaned by mechanical process; this coal is called "whole clean Powellton".

Results and Discussion

For the mass balance, the THF-solubles or liquids trapped in the coke were determined; the values have been normalized at 10g of coke. As is shown in Figure 1, as reaction time increases, liquids present in the coke decreases. This means that the contribution to the liquid yield from the coke is higher as reaction time is increased.

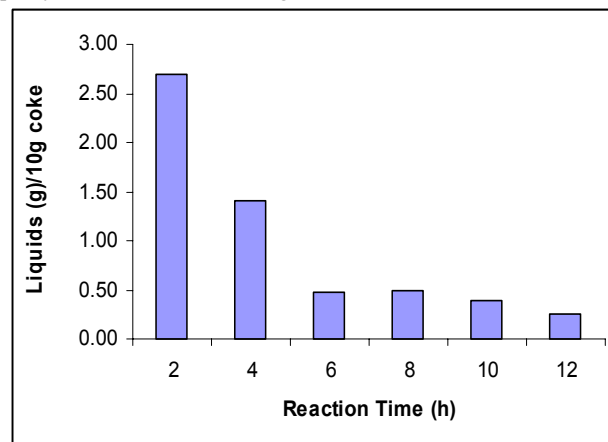


Figure 1. Variation of the liquids trapped in the coke (g)/10 g of coke with the time

The THF-solubles present in the decant oil (100%) run at 6h are much higher than the solubles present at the same reaction time but with the blend decant oil/coal. The amount of THF-solubles is 2.64 g/10g coke (decant oil 100%); this amount is comparable to that from reaction time at 2 hours (blended). We can conclude that the addition of coal acts to reduce the liquids trapped in the coke (increasing of the liquid yield) at lower reaction times.

Figure 2 shows the boiling point of the fraction <350C (i.e., potential gasoline and jet fuel). It is observed that at zero reaction time the percentage of the boiling point at <350C is 5%. Then, the percentage reaches a maximum value at 2-4 h and slightly decreases at 10-12 h.

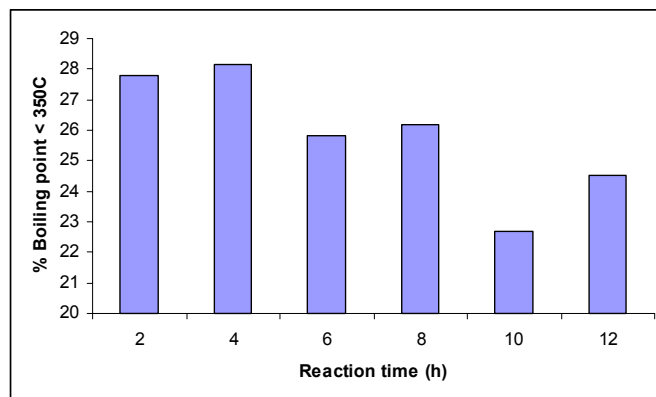


Figure 2. Fraction at boiling point <350C variation with the time

By comparing the boiling point fraction of the run at 6 h between decant oil (100%), 23.28%, and 2;1 decant oil:coal mixture,

25.80%, we can say that the additional 2.52% of the fraction <350C is provided by the coal volatiles. Therefore, the presence of the coal contributes to enhance the yield of the liquids at that specific cut point at 6h. The percentage of the particular cut <350C has been enhanced by 10% through the coal addition.

Conclusions

The addition of coal to the decant oil enhances the percentage of liquids to the fraction <350C. This indicates that the liquid obtained by the delayed coking process at laboratory scale contains coal-derived liquids, which provide cyclic and aromatics improving the stability of the jet fuel.

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References

- [1] Fickinger, A.E. *M.S. Thesis*. The Pennsylvania State University, University Park, PA. **2000**.
- [2] Eser, S.; Song, C.; Copenhaver, R.M.; Perison, J.; Schobert, H.H. *US Air Force Rept. AFWAL-TR-87-2042*, **1990**.
- [3] Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G. *Prepr. Pap.—Amer. Chem. Soc. Div. Petr. Chem.* **1992**, 37, 540.
- [4] Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G. *Energy Fuels* **1993**, 7, 234.
- [5] Coleman, M.M.; Schobert, H.H.; Song, C. *Chem. Britain*. **1993**, 29, 760.
- [6] Badger, M.W.; Santoro, R.J.; Schobert, H.H. *Newsletter, Intl. Assoc. Stabil. Handling Liq. Fuels*. **2001**, (26), 10.
- [7] Martin, S.C.; Tomic, J.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1997**, 42, 121.
- [8] Martin, S.C.; Tomic, J.; Schobert, H.H. *Proc. 9th Intl. Conf. Coal Sci.* **1997**, 3, 1557.
- [9] Badger, M.W.; Fickinger, A.E.; Martin, S.C.; Mitchell, G.D.; Schobert, H.H. *Proc. 8th Austral. Coal Sci. Conf.* **1998**, 245.
- [10] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1999**, 44, 106.
- [11] Butnark, S.; Badger, M.W.; Schobert, H.H. *Prepr. Pap. Amer. Chem. Soc. Div. Fuel Chem.* **1999**, 44, 662.
- [12] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **1999**, 44, 684.
- [13] Fickinger, A.E.; Badger, M.W.; Mitchell, G.D.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2000**, 45, 299.
- [14] Butnark, S.; Badger, M.W.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Petr. Chem.* **2000**, 45, 493.
- [15] Andréßen, J.M.; Strohm, J.J.; Boyer, M.L.; Song, C.; Schobert, H.H.; Butnark, S. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2001**, 46, 208.
- [16] Butnark, S.; Badger, M.W.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel. Chem.* **2001**, 46, 492.
- [17] Strohm, J.J.; Butnark, S.; Keyser, T.L.; Andréßen, J.M.; Badger, M.W.; Schobert, H.H.; Song, C. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2002**, 47, 179.
- [18] Badger, M.W.; Mitchell, G.D.; Herman, N.; Senger, B.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Fuel Chem.* **2002**, 47, 179.
- [19] Badger, M.W.; Butnark, S.; Wilson, G.R.; Schobert, H.H. *Prepr. Pap.—Amer. Chem. Soc. Div. Petr. Chem.* **2002**, 47, 198.
- [20] Butnark, S.; Badger, M.W.; Schobert, H.H.; Wilson, G.R. *Prepr. Pap.—Amer. Chem. Soc. Div. Petr. Chem.* **2002**, 47, 201.

A COAL TO HYDROGEN PLANT

Phil Amick, Global Energy Inc.
Robert Geosits, Bechtel Corporation
Sheldon Kramer, Nexant, Inc.

Introduction

In late 1999, as part of the Vision 21 program, the National Energy Technology Laboratory awarded Nexant, Inc. (a Bechtel-affiliated company) and Global Energy, Inc. (which acquired the gasification related assets of Dynegy Inc., of Houston, Texas including the E-GASTM gasification technology, formerly the Destec Gasification Process) a contract to optimize IGCC plant performance.¹ Task 1 of this contract developed optimized IGCC plant configurations: (1) petroleum coke gasification for electric power with/without the coproduction of hydrogen and industrial-grade steam, (2) coal gasification for electric power generation only, and (3) a Coal to Hydrogen Plant. Figure 1 is a schematic diagram of Task 1 showing the steps used to develop the various coal and petroleum coke gasification plants.

This paper summarizes the optimization and cost reduction techniques that were used, presents the optimized design, and describes plant performance. It also provides cost information and presents a financial analysis.

The Wabash River Coal Repowering Project

In 1990, Destec Energy, Inc. of Houston, Texas and PSI Energy, Inc. of Plainfield, Indiana formed the Wabash River Coal Gasification Repowering Project Joint Venture to participate in the Department of Energy's Clean Coal Technology Program by demonstrating the coal gasification repowering of an existing 1950's vintage generating unit. In September 1991, the project was selected by the DOE as a Clean Coal Round IV project to demonstrate the integration of the existing PSI steam turbine generator and auxiliaries, a new combustion turbine, a heat recovery steam generator, and a coal gasification facility to achieve improved efficiency and reduced emissions. In July 1992, a Cooperative Agreement was signed with the DOE.² Under terms of this agreement, the Wabash River Coal Gasification Repowering Project Joint Venture developed, constructed and operated the coal gasification combined cycle facility. The DOE provided cost-sharing funds for construction and a three-year demonstration period.

The participants jointly developed, separately designed, constructed, owned, and operated the integrated coal gasification combined-cycle power plant, using Destec's coal gasification technology to repower the oldest of the six units at PSI's Wabash River Generating Station in West Terre Haute, Indiana. The gasification process integrated a new General Electric 7FA combustion turbine generator and a heat recovery steam generator (HRSG) to repower the 1950s-vintage Westinghouse steam turbine

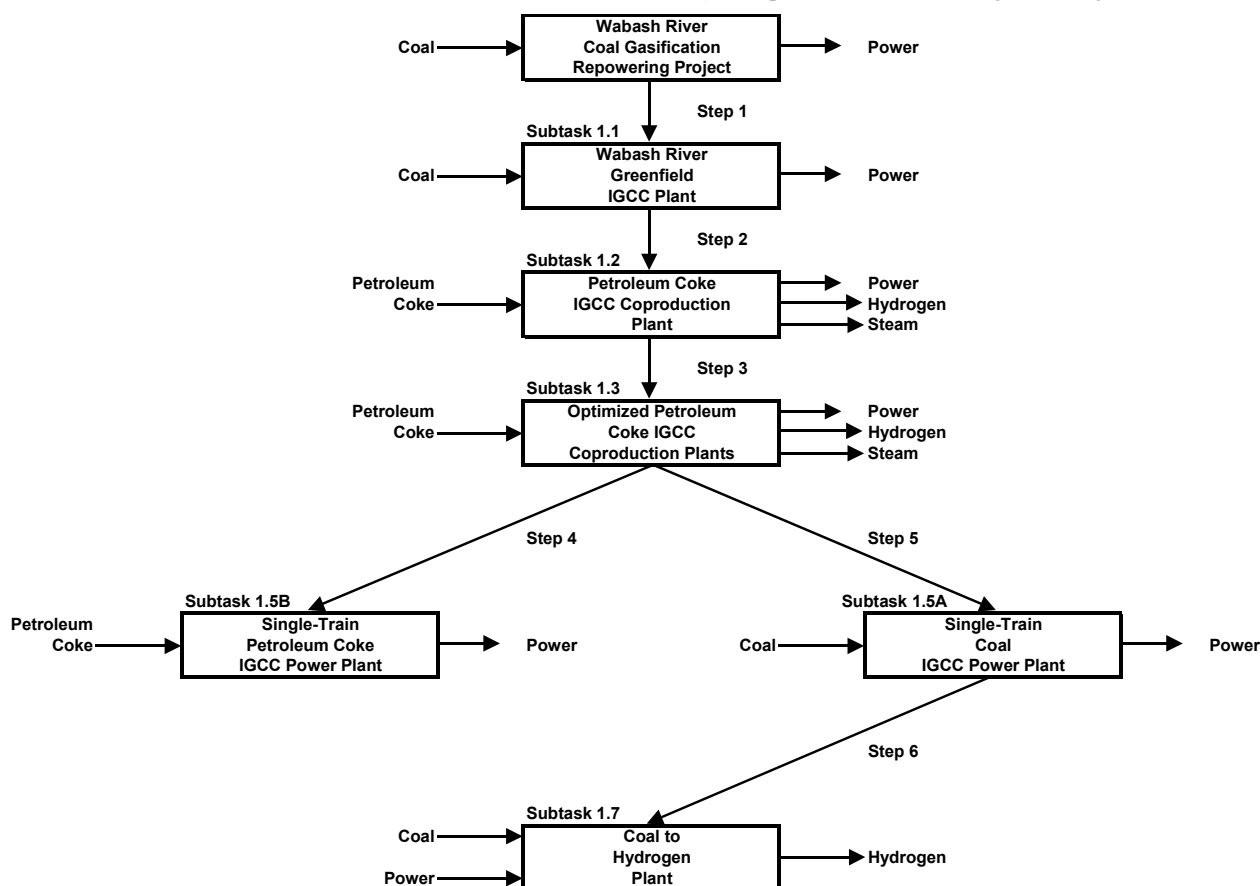


Figure 1. Schematic Diagram Showing the Chronological Development of the Coal to Hydrogen Plant

¹ Task 1 Topical Report, "Gasification Plant Cost and Performance Optimization," Contract No. DE-AC26-99FT40342, May 2002, <http://www.netl.doe.gov/coalpower/gasification/projects/systems/docs/40342R01.PDF>.

² Contract No. DE-FC21-92MC9310, "Wabash River Coal Gasification Repowering Project"

generator using some of the pre-existing coal handling facilities, interconnections, and other auxiliaries.

Based on the Wabash River Coal Gasification Repowering Project, Global Energy, Bechtel and Nexant contributed their combined design, engineering, construction, and operating expertise to develop optimized designs for state-of-the-art gasification plants for either coal or petroleum coke.

The Wabash River Greenfield Plant

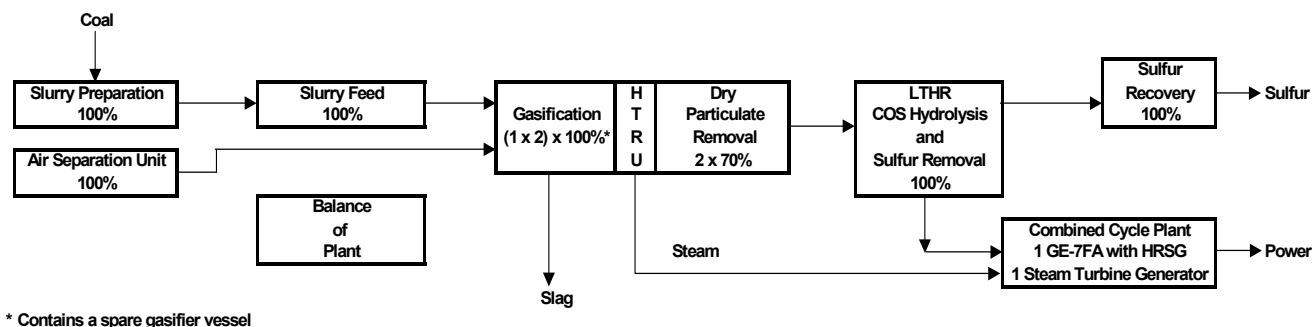
The gasification optimization work began by reviewing and assessing performance data and cost information from the existing Wabash River Project facility. From this basis, design and cost engineers adjusted the plant's scope – equipment, materials, and process operation – so that the Wabash River project design was transformed into a Greenfield IGCC design as shown in Step 1 of Figure 1. Figure 2 is a simplified train diagram showing the major process blocks in the Wabash River Greenfield Plant developed in Step 1. The plant processes 2,260 tpd of dry Illinois No. 6 coal and exports 269.3 MW of power. It also produces 356 tpd of slag and 57 tpd of sulfur. The export power of the greenfield facility is greater than the 262 MW of the Repowering Project because a newer steam turbine that is a better fit with the gasification block is used. The plant has a heat rate of 8,912 Btu (HHV)/kW-hr or a 38.3% thermal efficiency (HHV) to power.

Capital cost is a key part of IGCC economics and profitability. A three-stage cost estimating methodology was employed to develop a reliable mid-year 2000 total installed cost for the Greenfield Plant equivalent to the Wabash River Coal Gasification Repowering Project, but located at a generic site in a typical Mid-Western state.³ The plant would have an EPC cost of 452.6 MMS (mid-year 2000) or 1,680 \$/kW of export power. All plant costs cited in this paper are EPC costs which exclude contingency, taxes, licensing fees, and owners costs (such as land, operating and maintenance equipment, capital spares, operator training, and commercial test runs).⁴

The Optimization Process

Step 2, converted the Greenfield Plant to a petroleum coke IGCC coproduction plant located on the Gulf Coast. The next step optimized the petroleum coke IGCC plant. Process and project optimization was guided by Bechtel's Value Improvement Practices (VIPs) methodology using the following VIPs:

- Technology Selection



Note: Capacity percentages are based on total plant capacity

Figure 2. Simplified Block Flow Diagram of the Wabash River Greenfield Plant

³ Amick, P. et al., "An Optimized Petroleum Coke IGCC Coproduction Plant", Gasification Technologies Council Conference, San Francisco, CA, October 7-10, 2001.

- Process Simplification
- Classes of Plant Quality
- Process Reliability Modeling
- Design-to-Capacity
- Predictive Maintenance
- Traditional Value Engineering
- Constructability and Schedule Optimization

Initially, Bechtel and Global Energy prepared a Value Improvement Plan. This plan determined that the above practices were most applicable to this study. "Champions" were assigned to each applicable practice, and these champions along with the Value Improvement Plan administrator were responsible for implementation of the VIP process as well as documenting the results. Bechtel and Global Energy thoroughly analyzed the Value Engineering ideas generated during the brainstorming sessions to determine which were applicable for improving the project by assessing their benefits.

The VIP efforts were concentrated in the gasification area, specifically on the gasification and waste heat recovery section, the particulate removal section, the raw gas cooling area, and the syngas cleanup area. Lessons learned from plant operations showed that these areas are critical to reliable operations and high on-stream factors. In the Traditional Value Engineering VIP, almost 300 different ideas were generated in several brainstorming sessions. These ideas are based on (1) actual operations and maintenance experience at the Wabash River plant, (2) construction of the Wabash River Repowering Project, and (3) Bechtel's experience in other gasification and power generation projects with similar equipment. Personnel from the Wabash River facility proposed many of these ideas.

In conjunction with the Value Improvement Plan, Bechtel used the COMET plant layout program to evaluate and optimize equipment layout arrangements and minimize piping requirements for a given area or between areas. By changing the location of any piece of equipment in a given area, COMET readjusts the interconnecting piping and recalculates new quantities. This optimization tool is especially beneficial in cases where a large percentage of the piping is large bore or high cost alloy material. Additionally, the COMET program also is capable of automatically generating plot plans and three-dimensional architectural renderings of the plant.

⁴ These excluded items are included in the subsequent discounted cash flow financial analysis.

For several years now, Bechtel has been optimizing the heat integration of their standard coal and gas-based power plant designs. As a consequence, Bechtel has developed a *Powerline* suite of templates for combined cycle, pulverized coal, and fluidized bed power plant designs.⁵ These *Powerline* plants incorporate the most advanced technologies and best practices from Bechtel's engineering portfolio. Designing plants using standard templates saves engineering and procurement costs resulting in higher quality plants that are less expensive and require less time for construction. The lessons learned during the development of the *Powerline* templates also were applied to optimize the various subtask designs.

Bechtel has created a number of supplier alliances, not only for major equipment manufacture and fabrication, but also for bulk materials. In addition to reducing the price of equipment, these alliances also shorten the engineering and procurement cycle resulting in shorter overall project schedules and reduced EPC costs which translate into faster payback and increased profitability. These ideas also were applied to optimize the designs.

The resulting optimized Subtask 1.3 plant design has been previously described in Reference 3. Not only does the optimized petroleum coke coproduction plant have significantly improved performance, reduced emissions, and a substantially higher return on investment, it is 11% less costly than the original design.

The Subtask 1.5A Coal IGCC Power Plant

In Step 5, the design for a single-train coal-fueled IGCC power plant was developed based on the Subtask 1.3 Optimized Petroleum Coke IGCC Coproduction Plant. In this plant, the hot syngas leaving the gasifier goes to a hot residence vessel to allow further reaction. Following this, it is cooled in the high temperature heat recovery (HTHR) section before most of the particulates (98+%) are removed from the syngas by a cyclone. The remaining particulates and water

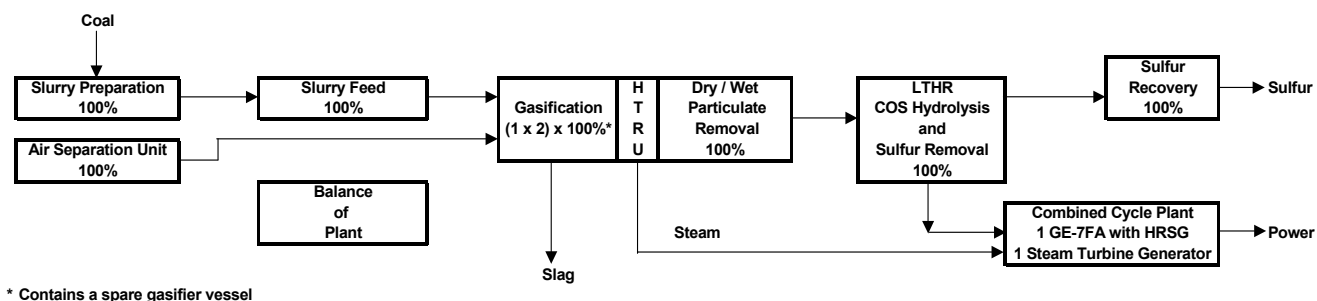
soluble impurities are removed simultaneously by wet scrubbing with water. The particulates are concentrated and recovered from the wash water by a filter system before being recycled to the gasifier for further reaction. Filtered water is recycled to the wet scrubber or is sent to the sour water stripper.

Figure 3 is a train diagram of the Subtask 1.5A Coal IGCC Power Plant. The plant consumes 2,335 TPD of dry Illinois No. 6 coal and produces 284.6 MW of export power, 60 TPD of sulfur, and 364 TPD of slag. The plant has a heat rate of 8,717 Btu (HHV)/kW-hr, or a 39.1% thermal efficiency (HHV). The plant cost 375 MM\$ (mid-year 2000) or 1,318 \$/kW of export power.⁶ Additional improvements have been identified to further reduce the plant cost.

The Subtask 1.5A Single-Train Coal IGCC Power Plant costs over 75 MM\$ less than the Subtask 1.1 Greenfield Plant and produces more export power showing the result of the optimization process and use of a larger and more efficient combustion turbine. On a \$/kW basis, the Subtask 1.5A plant costs over 22% less than the Subtask 1.1 plant. Furthermore, the Subtask 1.5A plant is less polluting than the Wabash River Greenfield Plant. On a lb/MW-hr basis, SO₂ is reduced by 56%, CO is reduced by 33%, and NO_x is reduced by 60%. Sulfur removal is increased from 96.8% to 98.5%.

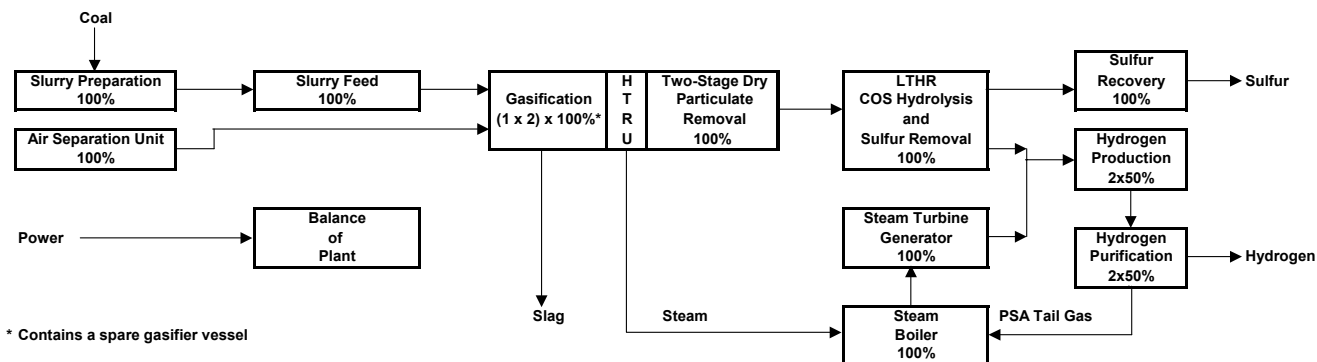
The Subtask 1.7 Coal to Hydrogen Plant

The gasification section of the Subtask 1.7 Coal to Hydrogen Plant produces 142 MMscfd of 99.0% hydrogen from 3,007 TPD of dry Illinois No. 6 coal. It also produces 76 TPD of sulfur and 474 TPD of slag, and consumes 18.4 MW of imported power. The plant satisfies all applicable environmental laws. The plant occupies about 38 acres. Figure 4 is a simplified block flow diagram of the Subtask 1.7 Coal to Hydrogen Plant



Note: Capacity percentages are based on total plant capacity

Figure 3 Simplified Block Flow Diagram of the Subtask 1.5A Single-Train Coal IGCC Plant



Note: Capacity percentages are based on total plant capacity

Figure 4. Simplified Block Flow Diagram of the Subtask 1.7 Coal to Hydrogen Plant

⁵ *Powerline* is a registered trademark of the Bechtel Corporation.

The Air Separation Unit (ASU) supplies about 2,522 TPD of 99.5% oxygen to Global Energy's two-stage E-GASTM gasifier which employs full slurry quench to control the second stage outlet temperature. The plant contains a spare gasifier vessel that can be placed in service to minimize the downtime whenever refractory replacement is required.

Char and unreacted coal particles that leave the gasifier in the syngas are collected downstream and recycled back to the first stage of the gasifier. Coal slurry, recycled char and oxygen are fed substoichiometrically into the first stage at elevated temperature and pressure to produce hot, raw syngas. Additional coal and slurry is added in the second stage, lowering the temperature of the gas through quenching and endothermic reactions; thereby, generating more syngas with a higher heating value. Particulates are removed from the syngas in a two-step system. First, a hot cyclone removes over 90% of the particulates, and the remainder is removed by an advanced dry char filtration system.

A Rectisol system is used for acid gas removal rather than an amine system for two reasons. First, it provides better sulfur removal from the syngas than an amine system so that a "sweet" shift process can be used to produce hydrogen from the CO in the syngas. The "sweet" CO shift system has the advantage of allowing higher CO conversions than the "sour" shift process. Secondly, the Rectisol system can be used to remove the bulk of the CO₂ from the shifted syngas for possible sale or sequestration, and it allows the downstream PSA unit to produce a 99.0% pure hydrogen stream containing only trace amounts of CO. However, a Rectisol system is more expensive and auxiliary power intensive than the amine systems that are used for the other subtasks.

The hydrogen production area consists of two parallel trains. Each train contains three CO shift reactors in series with cooling between them. The first two reactors are high temperature shift reactors that are sized to control the maximum outlet temperature. The third reactor is a low temperature reactor for maximum conversion. CO conversion is over 99%.

After the bulk of the CO₂ has been removed by the second stage of the Rectisol unit, two parallel PSA units purify the hydrogen. Hydrogen recovery from the shifted syngas is 90% to the 99.0% pure hydrogen product.

PSA sweep (off) gas is used to generate steam for the steam turbine. Medium pressure steam is extracted from the steam turbine for the CO shift reactors. The steam turbine produces 70.6 MW of power. The internal power consumption of the plant is about 89.0 MW. Thus, the plant imports about 18.4 MW of power. Table 1 shows the design feed and product rates for the Subtask 1.7 Coal to Hydrogen Plant.

The Coal to Hydrogen Plant has low emissions. The CO₂ vent gas emissions are free of SO_x and NO_x. However, the vent gas contains 0.51 mole% CO. At a 3% oxygen concentration and on a dry basis, the incinerator and steam boiler stack emissions contain 84 ppmv SO_x, 40 ppmv NO_x, and 50 ppmv CO. Combined, both stacks result in total emissions of 37 lb/hr of SO_x (as SO₂), 27 lb/hr of NO_x (as NO₂), and 1,846 lb/hr of CO. Sulfur removal is 98.5%.

The Coal to Hydrogen Plant costs 529.8 million mid-year 2000 dollars.⁶ This EPC cost is about 3.7 MMS per MMscfd of hydrogen production. Cost reductions could be obtained by relaxing the CO specification in the product hydrogen thereby allowing the use of a lower cost MDEA acid gas removal system. The cost of the

hydrogen plant on a per unit of hydrogen also could be lowered by building larger, multiple train plants or coproduction plants where electric power is the major product as was done in the Subtask 1.3 Petroleum Coke IGCC Coproduction Plant.

Table 1. Design Feed and Product Rates of the Subtask 1.7 Coal to Hydrogen Plant

Ambient Temperature, °F	59
Coal Feed, as received, TPD	3,517
Dry Coal Feed to Gasifiers, TPD	3,007
Total Fresh Water Consumption, gpm	2,457
Hydrogen, 99.0%, MMscfd	142.1
Sulfur, TPD	76.4
Slag Produced, TPD (15% moisture)	474.3
Total Oxygen Feed to the Gasifier, TPD of 99.5% O ₂	2,507
Heat Input to the Hydrogen Plant (HHV), Btu/hr x 10 ⁶	3,195
Cold Gas Efficiency to Clean Syngas (HHV), %	76.5
Steam Turbine Output, MW	70.6
Gasification Plant Power Consumption, MW	(53.6)
ASU Power Consumption, MW	(35.4)
Net Power Consumption (Power Import), MW	(18.4)

Availability. In Table 5.0A of the Final Report for the Wabash River Wabash River Repowering Project, Global Energy reported downtime and an availability analysis of each plant system for the final year of the Demonstration Period.⁷ During this March 1, 1998 through February 28, 1999 period, the plant was operating on coal for 62.37% of the time. There were three scheduled outages for 11.67% of the time (three periods totaling 42 days), and non-scheduled outages accounted for the remaining 25.96% of the time (95 days).

After adjustments, this data was used to estimate the availability of the Coal to Hydrogen Plant using the EPRI recommended procedure.⁸ Table 2 presents the design (stream day), average availability, and average daily (calendar day) input and product rates for the Coal to Power Plant. As the table shows there are significant differences between the calendar day rates and the stream day rates for all the input and output flows. The average hydrogen production rate is 116.7 MMscfd or 81.32% of the design rate.

Discounted Cash Flow Financial Analysis. A financial analysis was performed using a discounted cash flow (DCF) model that was developed by Nexant Inc. (formerly Bechtel Technology and Consulting) for the DOE as part of the Integrated Gasification Combined Cycle (IGCC) Economic and Capital Budgeting Practices Task.⁹ This model calculates investment decision criteria used by industrial end-users and project developers to evaluate the economic feasibility of IGCC projects. The IGCC financial model consists of 18 coupled spreadsheets in a Microsoft Excel workbook format. The model spreadsheets are organized into four main sections; (1) data input sheets, (2) supporting analysis sheets, (3) financial statements, and (4) projects summary result sheets.

⁷ "Wabash River Coal Gasification Repowering Project, Final Technical Report," U. S. Department of Energy, Contract Agreement DE-FC21-92MC29310, http://www.lanl.gov/projects/cctc/resources/pdfs/wabsh/Final%20_Report.pdf, August 2000.

⁸ Research Report AP-4216, *Availability Analysis Handbook for Coal Gasification and Combustion Turbine-based Power Systems*, Research Project 1800-1, Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA, August 1985.

⁹ Nexant, Inc., "Financial Model Users Guide – IGCC Economic and Capital Budgeting Evaluation," Report for the U. S. Department of Energy, Contract No. DE-AM01-98FE64778, May 2000.

⁶ All plant EPC costs mentioned in this report are mid-year 2000 order of magnitude cost estimates which exclude contingency, taxes, licensing fees, and owners costs (such as land, operating and maintenance equipment, capital spares, operator training, and commercial test runs). It also assumes that process effluent discharge is permitted.

Table 2. Design and Daily average Feed and Product Rates of the Subtask 1.7 IGCC Coal to Hydrogen Plant

Inputs	Design Rate	Daily Average Rate
Dry Coal, TPD	3,007	2,470
Electric Power, MW	18.4	15.1
River Water, gpm	2,457	2,018
Products		
Hydrogen, 99.0%, , MMscfd	142.1	116.7
Sulfur, TPD	76.4	62.8
Slag, TPD (15% moisture)	464.3	389.6
CO ₂ , TPD	7,125	5,795

At the base economic conditions shown in Table 3, the Subtask 1.7 plant requires a hydrogen selling price of 2.790 \$/Mscf to generate a 12% return on investment. These conditions are based on an 80% loan amount at a 10% interest rate with a 3% up front financing fee.

Table 3 shows the sensitivity of some individual component prices and financial parameters for the Subtask 1.7 Coal to Hydrogen Plant starting from a 12% ROI (with a hydrogen price of 2.79 \$/Mscf). Each item was varied individually without affecting any other item. Most sensitivities are based on a $\pm 10\%$ change from the base value except when either a larger or smaller change is used because it either makes more sense or it is needed to show a meaningful result. The hydrogen selling price has the greatest impact on the ROI with a 10% increase resulting in a 4.32% increase in the ROI to 16.32%, and a 10% decrease resulting in a 4.59% decrease in the ROI to 7.41%. Changes in the sulfur and slag prices have only a small influence on the ROI.

A 10% decrease in the dry coal price of 2.2 \$/ton from the base price of 22.0 \$/ton to 19.8 \$/ton will increase the ROI by 0.62% to 12.62%, and a 10% increase in the coal price to 24.2 \$/ton will lower the ROI by 0.62% to 11.38%. A 10% change in the imported power price has a lesser effect on the ROI.

A 5% decrease in the plant EPC cost to 503.3 MM\$ will increase the ROI by 1.59% to 13.58%, and a 5% increase in the plant cost to 556.3 MM\$ will decrease the ROI by 1.45% to 10.55%. A 10% change in the plant cost will have about double the effect of a 5% change

The loan interest rate is the most sensitive of the financial parameters that were studied. A 20% decrease in the loan interest rate to 8% from the base interest rate of 10% will increase the ROI to 15.30% from 12.00%, and a 20% increase in the interest rate to 12% will lower the ROI to 8.68%. A 20% decrease in the loan amount from 80% to 72% will lower the ROI by 0.52% to 11.48%, and a 20% increase in the loan amount to 88% will increase the ROI by 0.83% to 12.83%. Decreasing the income tax rate by 10% from 40% to 36% will increase the ROI to 12.48%, and a 10% increase in the tax rate to 44% will lower the ROI by 0.52% to 11.48%.

Effect of Loan Interest Rate. At a 8% loan interest rate and with the 3% up front financing fee, a 12.0% ROI can be obtained at a hydrogen selling price of 2.590 \$/Mscf. This is a drop of 0.20 \$/Mscf from the 2.790 \$/Mscf price required with a 10% loan interest rate. Figure 5 shows the effect of the hydrogen selling price on the ROI for the Subtask 1.7 Coal to Hydrogen Plant at both 8% and 10% loan interest rates. The two curves are very similar with the ROI for the 8% loan interest rate having about 3.3% higher return than that for the 10% loan interest rate.

Table 3. Sensitivity of Individual Component Prices and Financial Parameters for the Subtask 1.7 Coal to Hydrogen Plant Starting from a 12% ROI (with a Hydrogen Price of 2.79 \$/Mscf)

Products	Decrease			Base Value	Increase		
	ROI	Value	% Change		% Change	Value	ROI
Hydrogen	7.41%	2.511 \$/Mscf	-10%	2.790 \$/Mscf	+10%	3.069 \$/Mscf	16.32%
Slag	11.80%	-5 \$/t	---	0 \$/t	---	5 \$/t	12.20%
Sulfur	11.98%	27 \$/t	-10%	30 \$/t	+10%	33 \$/t	12.02%
Feeds							
Coal	12.62%	19.8 \$/t	-10%	22.00	10%	24.2 \$/t	11.38%
Power	12.12%	24.3 \$/MW-hr	-10%	27.0 \$/MW-hr	+10%	29.7 \$/MW-hr	11.88%
Financial							
EPC Cost	13.58%	503.3 MM\$	-5%	529.8 MM\$	+5%	556.3 MM\$	10.55%
EPC Cost	15.29%	476.8 MM\$	-10%	529.8 mm\$	+10%	582.8 MM\$	9.20%
Interest Rate	15.30%	8%	-20%	10%	+20%	12%	8.68%
Loan Amount	11.48%	72%	-20%	80%	+20%	88%	12.83%
Tax Rate	12.48%	36%	10%	40%	+10%	44%	11.48%

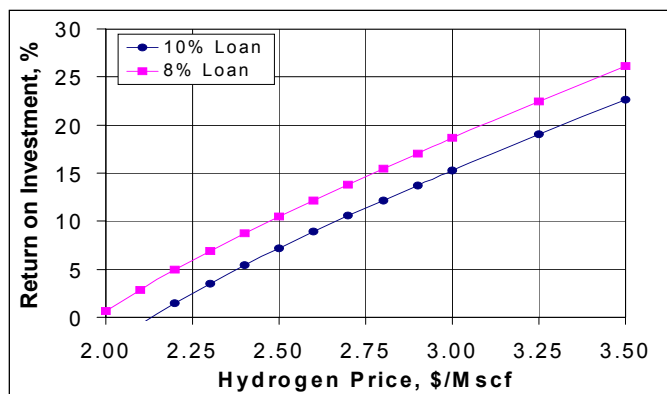


Figure 5. Effect of Hydrogen Selling Price on the Return on Investment

Effect of Syngas Availability. After commissioning all plants undergo a “learning curve” during which problem areas are corrected, inadequate equipment is replaced, and adjustments are made. Consequently, performance improves as measured by increased capacity and/or improved on-stream factors. At a 10% loan interest rate, Figure 6 shows the effect of improved hydrogen availability on the ROI for the plant at a hydrogen selling price of 2.79 \$/Mscf. Increasing the hydrogen availability from the expected 81.3% to 85% increases the ROI to 13.68% from 12%.

Figure 7 shows the effect of improved hydrogen availability on the required hydrogen selling price for a 12% ROI for both 8% and 10% loan interest rates. Increasing the hydrogen availability from 81.3% to 85% reduces the required hydrogen selling price by about 0.10 \$/Mscf in each case.

These two figures show the importance of designing, constructing and operating the plant to obtain a high hydrogen availability. Care should be taken in the design and selection of process equipment so that they will have a high reliability and require minimum scheduled downtime for maintenance.

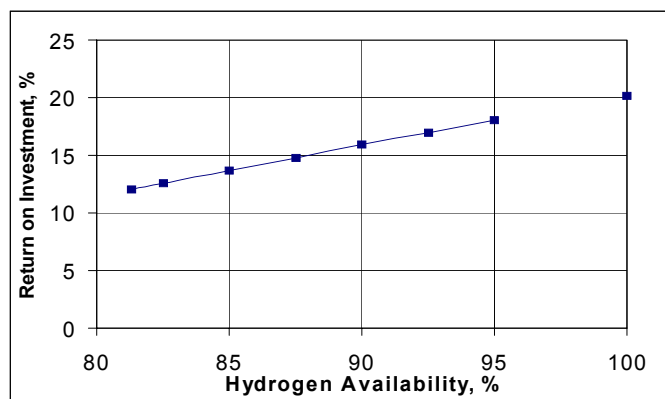


Figure 6. Effect of Hydrogen Availability on the Return on Investment with Hydrogen Price of 2.79 \$/Mscf and a 10% Loan Rate

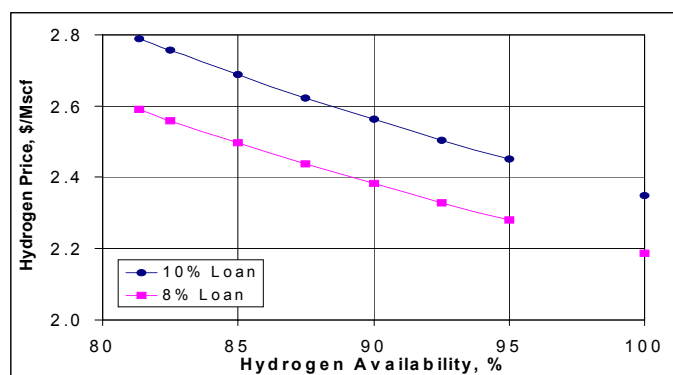


Figure 7. Effect of Hydrogen Availability on the Required Hydrogen Selling Price for a 12% Return on Investment

Effect of Plant Cost. Figure 8 shows the effect of the plant EPC cost on the required hydrogen selling price for the plant to produce a 12% return on investment. At a 10% loan rate, a 5% reduction in the plant EPC cost from 529.8 MM\$ to 503.3 MM\$ will reduce the required hydrogen selling price from 2.790 \$/Mscf to 2.695 \$/Mscf, a reduction of about 0.09 \$/Mscf or 3.4%. At a 8% loan interest rate, a 5% reduction in the EPC cost reduces the required hydrogen selling price from 2.590 \$/Mscf to 2.505 \$/Mscf, a reduction of about 0.08 \$/Mscf or 3.3%.

Summary

The objective of this study was to design a single-train coal to hydrogen plant. The design presented in this report satisfies that objective. It processes 3,007 TPD of dry Illinois No. 6 coal and produces 142.1 MMscfd of 99.0% hydrogen at 1,000 psig. It has an installed cost of 529.8 million mid-year 2000 dollars.

For the plant to generate a 12% ROI, the required hydrogen selling price must be in the 2.50 to 2.80 \$/Mscf range. The exact value depends upon the financing assumptions. However, there are several possibilities for reducing the required hydrogen selling price.

First, the hydrogen purity specification can be relaxed allowing a higher concentration of oxygen containing impurities in the hydrogen. This would not be harmful if the hydrogen were to be used for hydrotreating in a refinery environment, but could be detrimental for certain petrochemical applications. In this situation, the Rectisol system would be replaced by an amine system, a "sour" shift would be employed, the hydrogen production would be reduced by 9.4%, the plant would become a net electric power producer

exporting 39 MW, and the capital cost would be reduced by about 58 MM\$. The net effect is that the required hydrogen selling price for a 12% ROI would drop by about 0.19 \$/Mscf to 2.60 \$/Mscf with a 10% loan interest rate.

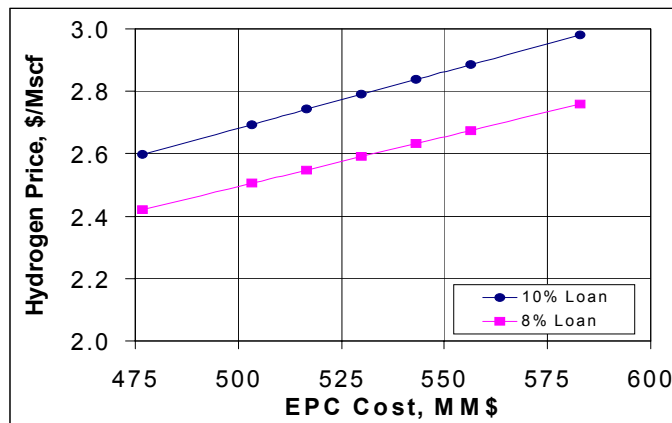


Figure 8. Effect of EPC Cost on the Required Hydrogen Selling Price for a 12% Return on Investment

Second, switching to the use of a lower cost fuel, such as petroleum coke, as was used in the Subtask 1.2 and 1.3 cases. Approximating this situation by using a zero cost coal would reduce the required hydrogen selling price for a 12% ROI by about 0.40 \$/Mscf.

Third, instead of using a single gasification train with a spare gasifier vessel, a complete spare gasification train (without a spare gasifier vessel) could be installed to increase the hydrogen availability. Although this would increase the plant cost, the hydrogen availability would be increased to about 91.7%, and the required hydrogen selling price for a 12% ROI would drop by about 0.11 \$/Mscf to 2.684 \$/Mscf. This design philosophy was demonstrated during the Subtask 1.3 studies (see references 1 and 3).

Fourth, if the plant were located where the captured CO₂ could be utilized for enhanced oil recovery, the economics would be substantially improved. Assuming the CO₂ could be sold for 12 \$/ton, the required hydrogen selling price for a 12% ROI would drop by about 0.6 \$/Mscf to 2.194 \$/Mscf.

By combining three of the above cases (1. the zero cost feedstock, 2. the increased availability of a spare gasification train, and 3. the opportunity to sell CO₂ for enhanced oil recovery) with an 8% loan rate will significantly reduce the required hydrogen selling price for a 12% ROI to about 1.50 \$/Mscf.

Building a larger plant with coproduction of power (similar to that of Subtask 1.3) should allow the advantages of economies of scale primarily by reducing the apportioned cost of the utilities and other OSBL areas that are attributable to the hydrogen plant. Also, a multiple train plant would provide a more reliable source of some hydrogen (although not at the rated capacity) since it is unlikely that the entire plant would be shut down at the same time. This should make the cost of hydrogen competitive with that from steam methane reforming of natural gas.

CLEAN AND EFFICIENT COAL BASED ELECTRIC POWER GENERATION

Janos M. Beér

Department of Chemical Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave
Cambridge, MA., 02139 USA

Background

The provision of electric power is one of the prerequisites of prosperity; there is strong correlation between electric power generating capacity and per capita GDP. Because of the large coal reserves in the major developing countries such as China, India and Indonesia, where most of the new power generating plants will be installed, it can be expected that coal will remain the dominant source of power generation world wide, at least during the first half of this century. According to US Energy Information Administration data for 1999,¹ of the around 800 GW electric power generating parks in the USA, 54% are fueled by coal, 16% by natural gas (increasing to an estimated 36% by 2020), and about 1% by oil. The rest are by nuclear power (18%), hydro power (9%), and by renewable solar, wind or biomass (2%). Across the world economic indicators signal continued growth and increased electricity demand. 1200 GW of new capacity is projected during the next fifteen years to be added to the world's present electric generating capacity of about 3500 GW. A large proportion of this new capacity will be installed in China, India and Indonesia, and will be coal based. Coal as an energy source has the advantages of broad availability with large reserves in several countries over the world, safe and secure supply, low cost, and economic utilization by mature technologies. The disadvantages are due mainly to combustion generated pollution. Clearly, as coal is going to be used in the future it has to be used cleanly and efficiently, to minimize adverse environmental impact.

Pollutant Emission Control

In the 1970s, applied combustion research has taken a turn from high output, high intensity combustion towards combustion process modifications for reduced pollutant emissions. The combustion generated pollutants of concern are oxides of sulfur, of nitrogen and carbon, and fine organic and inorganic particulates (**Figure 1**).

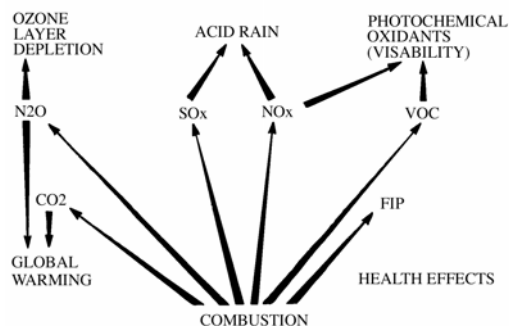


Figure 1. Combustion Generated Pollutant Emissions.

Sulfur in the coal oxidizes during combustion mainly to SO_2 , an acid rain precursor. Methods of sulfur capture in the combustion process involve the reactions of additive sorbents such as calcined limestone, CaO , with SO_2 to produce CaSO_4 , a stable, disposable

solid waste. In the high temperature, fuel-lean environment of pulverized coal flames ($T_{\text{peak}} \sim 2000\text{K}$), however, CaSO_4 is unstable; it decomposes, which leaves flue gas desulfurization as the viable option of sulfur capture in PC combustion.

The development of Fluidized Bed Combustion (FBC) for steam generation, in the 1960s² provided the opportunity to retain sulfur in the combustion process, because CaSO_4 is stable at FBC operating temperatures of 1050-1170K. One of the difficulties of FBC technology is that it does not lend itself well to scale-up to the 700-1000 MW utility size range, mainly because of the large number of feed points it requires to ensure uniform distribution of the coal across the fluidized bed. Conditions for scale up are more favorable in Circulating Fluidized Bed Combustion (CFBC) where the gas velocities are higher and the cross sectional area of the bed for a given thermal performance of the boiler is smaller than for a conventional bubbling fluidized bed. This, on the other hand, helps to reduce the number of coal feed points, which is an operational convenience. Also, smaller size limestone particles can be used which improves the sulfur capture and reduces the Ca/S mole ratio necessary for reaching a target value of sulfur capture, typically 90-95%.

Sulfur dioxides emissions from utility plants in the U.S. have been reduced 40% since 1980 even though electricity production increased by 35% during the same period. This was achieved by switching to coals of lower sulfur content, and by retrofitting some of the existing coal fired power plants with scrubbers. This process will have to continue to satisfy the constraints of the Clean Air Act Amendment 1990 which require further continuing reductions in SO_2 emissions in its Phase 2 implementation that began in the year 2000.

Nitrogen oxides as pollutants deserve special attention because of their wide ranging effects on the environment, including contribution to acid rain, reduction of atmospheric visibility, production of tropospheric ozone, and in the case of N_2O , depletion of stratospheric ozone. It is also noteworthy that NO_x emissions are well amenable to reduction by combustion process modifications;³ nitrogen compounds organically bound in the coal and NO_x formed in the course of combustion can be converted to molecular nitrogen in fuel-rich pyrolysis reactions. The chemistry of nitrogen compound interconversions in high temperature coal pyrolysis, and of NO formation in fuel lean combustion⁴ are the bases of the design protocol for low NO_x combustion technology.

In coal combustion, where the major part of the NO_x is formed by the oxidation of nitrogen compounds organically bound in the coal, the design protocol requires:

- sequential fuel-rich and fuel-lean combustion zones achieved by staged air or staged fuel supply to the combustion process,
- maintenance of high temperature in the fuel-rich flame zones, and
- reduced peak flame temperatures in fuel-lean flame regions.

Low NO_x combustion technologies include: Over Fire Air (OFA), low NO_x Burners (LNB), and NO Recburn.

In the method of **Over Fire Air (OFA)** a fuel-rich pyrolysis zone is created in the lower part of a furnace with only 70-80% of the stoichiometrically required combustion air. For effective conversion of the fuel nitrogen to N_2 , high temperature and sufficient residence time for the pyrolysis reactions to run their course ($>300\text{ms}$), are required. The rest of the combustion air needed for complete combustion is then injected in the upper furnace in the form of high velocity air jets (OFA). Fast admixing of the overfire air can reduce the formation of thermal NO during this fuel-lean combustion stage. OFA is capable of reducing NO_x by 40-60% from uncontrolled

emission levels. To date, approximately 39 GWe coal fired capacity in the USA has been fitted with OFA.

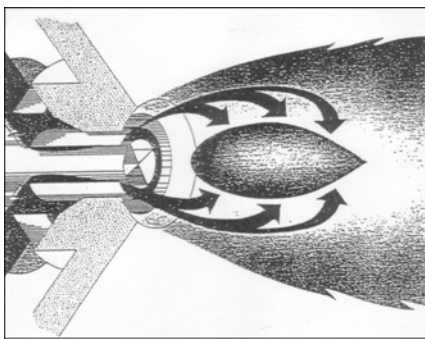


Figure 2. Low NOx Burner Schematic

In **Low NOx Burners (LNB)** the staged admixing of air to the pulverized coal jet occurs by aerodynamic control (**Figure 2**). Both the fuel and the air are introduced through the same burner. Application of Low NOx Burners can reduce emissions typically by 50%. There are a number of engineering designs that offer retrofits with no changes to pressure parts, and minimal or no changes to wind boxes of the boilers. LNBs represent the most cost effective NOx reduction technology. Since 1995, more than 35 GWe of a total of 325 GW coal fired capacity in the USA has been retrofitted with LNBs.⁵

In **NOx Reburning** the NOx reduction is effected by the injection of a hydrocarbon fuel, about 15-20% of the total heat input, into the fully burned combustion products of the coal flame.⁶ NOx can be reduced by about 60% in the slightly fuel rich flame created by the injection of the reburning fuel. Tertiary air has then to be added for completing combustion. The Reburning fuel can be Natural Gas or a High Volatile Bituminous Coal. NO reburning technology has been successfully applied in the USA for cyclone fired boilers,⁷ and for wall- and tangentially-fired pulverized coal combustion with dry ash removal.⁸ The above mentioned technologies can be effectively combined to increase NOx reductions:

LNBs	30-55%
LNB+OFA	35-70%
Reburning (Nat.gas)	~60%
LNB+Reburning (Nat.gas)	60-70%

The reduction of NOx emission by combustion process modification, a science based technology, has been successfully applied in industry; more than 188 GW of electric power generating capacity currently in operation internationally has been fitted by these "primary combustion measures".⁵

Further reductions in NOx emissions can be obtained by the injection of additive ammonia into the combustion products. At high temperature (1060K-1350K) no catalyst is needed in the **Selective Non Catalytic Reduction (SNCR)** process for the removal of up to 40% of the NO formed during coal combustion.

In **Selective Catalytic Reduction (SCR)** the ammonia vapor is injected over a catalyst bed situated at the boiler economizer outlet where the flue gas temperature ranges from 600K to 650K. In the presence of the catalyst, the ammonia chemically reacts with NOx to form water vapor and N₂. The costs of SRC installation are higher than that of the SNCR, but much less ammonia has to be injected, and NOx reductions in excess of 90% can be obtained, depending on the type of coal burned.

Coal based high efficiency power cycles

The efficiency of existing power plants in the U.S. is in the range of 33-36%. Advanced cycles of power generation, some of them mature technologies, others at the stage of demonstration or R&D, hold the promise to generate electricity at significantly increased efficiency (in the range of 50% and above). These technologies ought to be commercially available in the U.S. soon, as it will be necessary to replace older plants beginning 2010. Higher efficiency is the key to the reduction of all of the pollutants and is presently the practical route for mitigating CO₂ emissions. In the near term there are several options for clean and efficient electric power generation, including the following technologies:

- Pulverized coal combustion (PCC) in Supercritical steam boiler in a single Rankine Cycle (4500 PSI/2x 1200F),
- Pressurized Fluidized Bed (PFBC) with Topping Combustor,
- Integrated Gasification Combined Cycle (IGCC) with coal, refinery waste, or biomass as fuel.

Pulverized coal fired supercritical steam boilers have been in use since the 1930s but improvements in materials and increasing demand for higher efficiency are making this system presently the choice of new coal fired utility plant world wide. The increase in efficiency is due to the higher mean temperature of heat addition in the supercritical steam cycle. Comparison of design parameters of a new 300 MW subcritical steam cycle plant with a supercritical plant of the same performance shows an efficiency gain of 1.7% with a fuel saving of 50,000t/y and a CO₂ emission reduction of 137,000t/y for the supercritical unit.⁹ The efficiency of a pulverized coal fired steam plant can be increased in small steps to beyond 45% using supercritical steam parameters as shown in **Figure 3**.¹⁰

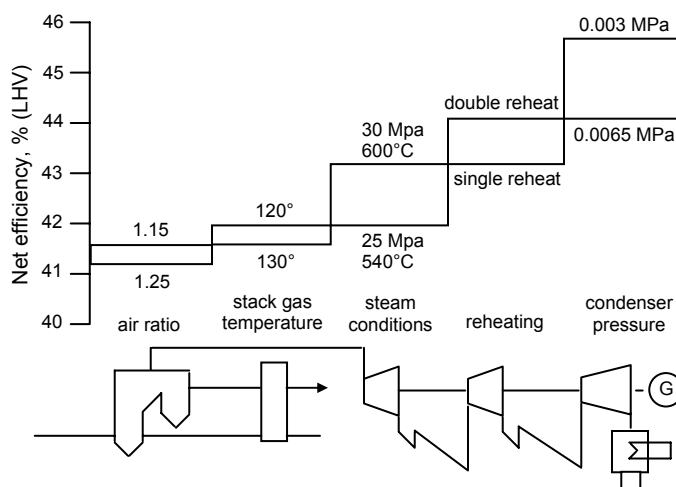


Figure 3. Improving efficiency in P.C. power plants.¹⁰

Pressurized Fluidized Combustion¹¹ has grown out of the early development at BCURA in Leatherhead UK in the 70s, the Grimethorp Experimental Facility in the UK in the 80s funded by Germany, the UK, the USA and the IEA; and R&D at the Stal Laval Company in Sweden in preparation of the 70MWe demonstration plant built for the American Electric Power Co. Compared to AFBC, the heat release rate per unit bed area in PFBC is about an order of magnitude higher, and the bed height is 3-4 meters instead of the typical bed height of 1 m in AFBC. Under atmospheric pressure conditions the bed height is limited by the acceptable pressure drop of about 100 mbar across the bed. In the PFBC-GT Cycle the 300 mbar pressure drop represents less than 3% of the total pressure ratio.

A consequence of the increased bed height is a larger carbon inventory in the bed and lower NO emission due to the reduction of the formed NO by solid carbon.¹² The high carbon load does not, however, reduce the emission of the N₂O which is still stable at the relatively low temperature of the PFBC. The temperature in the PFBC is also too low for an efficient gas turbine application. The thermodynamic efficiency of the PFBC Combined Cycle units in operation is about 40%.

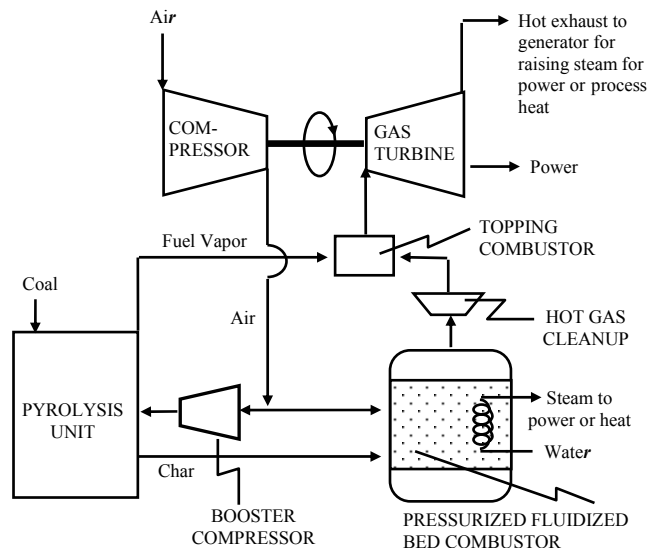


Figure 4. Pressurized Fluidized Bed Combined Cycle.

Further increases in efficiency can be obtained by the use of a **Topping Combustor**. In this latter cycle (**Figure 4**), coal, usually in the form of coal-water slurry is injected into a pressurized fluidized bed carbonizer where it undergoes partial gasification to produce a low calorific value gas, and char. The char is burned in a Pressurized Fluidized Bed (PFBC) and the flue gas is cleaned of particulates and

alkali at high temperature. Sulfur is captured both in the fluidized bed carbonizer and combustor by additive dolomite. The syngas produced in the carbonizer is cleaned of particulates and alkali by hot gas cleanup. It is then mixed with the oxygen rich combustion products of the PFBC in the Topping Combustor where it is burned to raise the temperature at the inlet to the gas turbine to 1623K. This temperature rise increases the cycle efficiency to about 47%. Further improvements in efficiency can be obtained by the application of advanced gas turbine technology, and on the steam side, by supercritical steam parameters with high temperature double reheat. An additional advantage of this cycle is that the N₂O emission is eliminated because the N₂O formed in the Pressurized Fluidized Combustor decomposes at the elevated temperature in the Topping Combustor.¹³

Integrated Gasification Combined Cycle (IGCC)

IGCC involves the total gasification of coal with oxygen and steam to produce a high calorific value fuel gas for combustion in a gas turbine. The gasifier also produces steam for a steam power cycle. The fuel gas has to be cleaned of particulates, alkali and sulfur compounds; the fuel-nitrogen bearing gas is burned in a low NO_x combustor. The main features of IGCC are shown in **Figure 5**.¹⁴

IGCC is the cleanest advanced coal technology. It is also demonstrated to be working with no major operational problems. The future of IGCC depends on whether it will be possible to reduce its first cost and to increase its cycle efficiency. The cost is presently high, mainly because of the oxygen plant necessary for the oxygen blown gasifier and because of the less than complete integration of the various subsystems such as the gasifier air separation system, fuel gas cooler and cleanup, gas turbine and steam plants.

Existing IGCC demonstration plants in the USA have design efficiencies of 40%, but two more recently commissioned European IGCC demonstration plants, the one in Buggenum in the Netherlands, and the other, the Puertollano plant in Spain, both of which began operation in 1993, have higher design efficiencies of 43% and 45%, respectively. The higher cycle efficiencies are due to improved gas turbine and steam plant efficiencies and better sub-system integration. An example of such an improved sub system integration

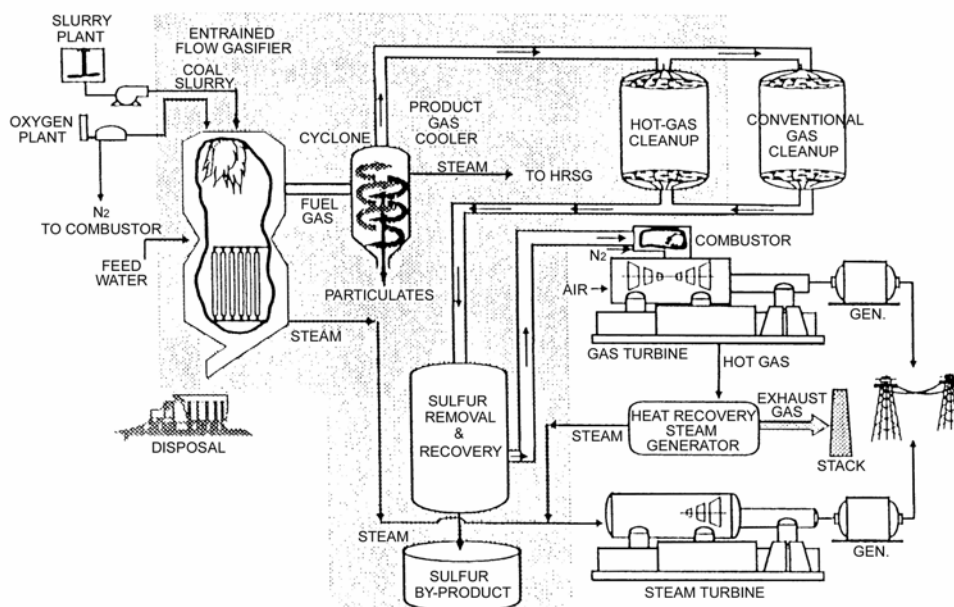


Figure 5. Integrated gasification combined cycle schematic.

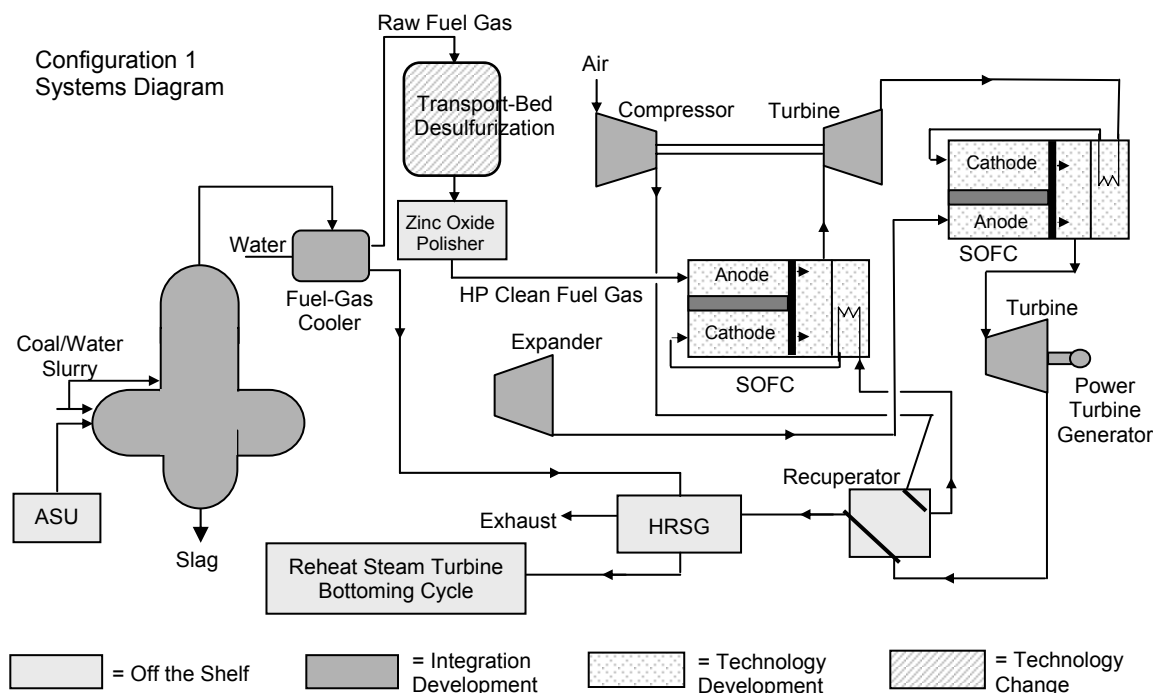


Figure 6. Vision 21 fuel cell / gas turbine cycle.

occurs at the boundary of the oxygen blown gasifier and the gas turbine combustor. The air separation unit produces oxygen for the gasifier in the Portollano plant at 13 bar pressure. The nitrogen, which is also available at high pressure, is mixed with the clean gas to feed the gas turbine combustors; this helps to control NO_x emission and increases the mass flow rate through the turbine raising thereby the turbine performance. The NO_x is further lowered through the saturation of the coal gas by water (condensate from the steam cycle) heated up by the sensible heat of the compressed air (673K) at the compressor outlet.

While the first cost of IGCC at present is higher than PC/supercritical steam, the balance may be tilted towards IGCC in the future because:

- IGCC lends itself for the efficient removal of mercury and CO₂ from the high pressure fuel gas;
- with the strongly increasing volume of refinery wastes (heavy residual oils, petroleum coke, Orimulsion) IGCC could become attractive for using fuels of very low or even "negative" cost. (The waste fuel cost is negative if it stands against the cost of disposal);
- the cycle efficiency could exceed 50% in schemes of producing hydrogen in the gasification process and combining the Brayton-Rankine Cycles with Fuel Cells. An example, the US DOE's Vision21 Gasification /Gas Turbine/Fuel Cell Cycle Schematic is shown in **Figure 6**.¹⁵

Table 1. Environmental performances at full load (mg/N m³, 6% O₂).

Technology	PCC + FGT	CFBC	PFBC	PCFBC	IGCC	TC
Nitrogen oxides						
Intrinsic	800-1300	150-250	200-300	100-200	150-200	150-300
Low-NO _x burners	400 ^a					
In project		75-120	70-200	40-100		
With SCR	100-200					50-150
Nitrous oxide	0-5	20-100	20-100	20-100	0-5	0-5
Sulfur dioxide (1.0% S)		^b	^b	^b		^b
Intrinsic	2000	200	200	200	10-25	200
Ca/S ratio	1.05	2.5	2.2	1.5		2.0
With FGD	200					
Dust	50	50	50	10 ^c	10 ^c	10 ^c

^a For new boilers 400mg/N m³; from 500 to 700 mg/N m³ for existing ones.

^b With ceramic filters.

^c It is possible to reach emission levels below 200 mg/N m³ by simply increasing the quantity of limestone injected into the furnace, and consequently the Ca/S ratio.

Comparison of Clean Coal Technologies

Several studies attempted to compare the emerging Clean Coal Technologies with PCC + Flue Gas Treatment from the points of view construction cost, operating cost, cost of electricity fuel flexibility, pollutant emission, and cycle efficiency (CO₂ emission). Efficiency is becoming an important factor as it is the main determinant of CO₂ emission. For a comparison of these technologies it is also important to forecast the development of some enabling technologies such as new superalloys for gas turbine blades and for superheaters in supercritical steam boilers.

It is generally agreed that PCC + FGT has an edge over the coal fired combined cycle systems in the short and medium term mainly because it is a mature technology and also because competition and R&D in recent years has reduced its first cost to below \$1100/kW installed capacity.

Comparisons of environmental performance data at full load (estimated by Delot et. al.¹⁶) are shown in **Table 1**. The low temperature fluid bed systems, except of the PFBC with Topping combustor, have a problem with N₂O emission while PCC may face some future regulation on fine particulate (PM 2.5) and HAP (e.g., mercury) emissions. IGCC is the potentially cleanest of the advanced coal fired cycles and has also the special advantage that it is amenable to the efficient capture of CO₂ from the high pressure syngas stream.. This is further underlined by the comparative illustration of environmental advantages of advanced power cycles shown in **Figure 7**.¹⁷ IGCC can be seen to have lower NO_x emission than a Gas Turbine Combined Cycle, and with sequestration its CO₂ emission compares also favorably with that from a natural gas fired combined cycle.

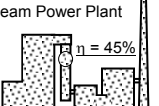
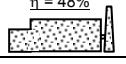


CO₂ Sequestration

In addition to current strategies of improving the efficiency of power generation, greenhouse gas emission can be mitigated by CO₂ sequestration.¹⁸ CO₂ capture and sequestration technology used to reduce the CO₂ concentration in North Sea natural gas is based on chemical absorption with monoethanolamine (MEA). This process is expensive and prohibitively wasteful in energy use for CO₂ capture

from flue gas in power plant. The problem of efficient CO₂ capture hinges on increasing the CO₂ concentration in, and reducing the volume flow rate of, the gas to be treated. There are combustion measures which by increasing the CO₂ concentration in the flue gas can reduce the costs associated with CO₂ separation. One such technique applicable to atmospheric-pressure boilers is oxygen enrichment of the combustion air and recirculation of high CO₂ bearing flue gas through the burners.¹⁹ While such a scheme has to bear the cost of an air separation unit to produce the oxygen, there is some compensation in the reduced volume of the flue gas, which reduces the cost of flue gas clean up equipment and improves the boiler efficiency. CO₂ capture becomes more favorable when the gas to be treated is at elevated pressure and is a syngas rather than flue gas, the product of partial or total coal gasification such as in the cases of PFBC with Topping Combustion or IGCC.

Conclusions

- Coal is the prevailing fuel of power generation world wide, and it is likely to remain important well into this century,
- Because of coal's pollution, and especially due to the expected future limitations on CO₂ emissions, clean coal utilization technology with high thermodynamic efficiency will have to be applied in the new generation of coal fired central power stations to be built in OECD countries.
- Pulverized Coal Combustion in Supercritical Steam Boilers (240atm 2x 838 K) is the likely choice for new central power plants in the short and medium term because of the relatively high efficiency (42-45% LHV) and the long experience with pulverized coal combustion. Also, the cost of these plants is continually getting reduced (presently about \$ 1100/kW) There are more than 30 SC plants being commissioned at present in Europe, Australia Japan, S.Korea and Taiwan. Further developments towards Ultra Supercritical Coal Plants (300 atm 3 x 923 K) with 50% single cycle efficiency is dependent on progress in materials R&D; applications are expected past 2010.

Coal/ Natural gas	Limestone		CO ₂	SO ₂	NO ₂	Ash	Gypsum	Rejected heat (Cooling water)
[g/kWh]			[g/kWh]	[mg/kWh]		[g/kWh]		[MJ/kWh]
320	12	Pulverized-Coal-Fired Steam Power Plant  η = 45%	770	560 *	560 *	32	19	4.0
300	22 **	Combined Cycle Power Plant with Pressurized Fluidized Bed Combustion  η = 48%	730	525 *	525 *	Ash / Gypsum / Limestone Mix 56 **		3.2
285		Integrated Coal-Gasification C.C. Power Plant  η = 50%	700	140	275	Slag 29	Sulfur 4	3.0
125		Natural-Gas-Fired C.C. Power Plant  η = 58%	345		315			2.3

* 200 mg/m³ Flue gas (STP, Dry basis, 6 vol. % O₂)

** Molar Ca/S-ratio = 2

Figure 7. Comparison of supply flows, emissions and byproducts of different 600 MW-class power plants.¹⁷

- Pressurized Fluidized Combustion Combined Cycle in several plants of 70 MWe have been operating satisfactorily since 1991 and a larger plant (360MWe) is starting up in 1999 in Japan. Low alkali coal permits the use of higher pressure ratio with 850C gas turbine entry temperature. Efficiency is around 40% (LHV). Emissions are low, except N₂O (50–100 ppm).
 - PFBC Topping Combustor Cycle Pregasification produced syngas raises turbine inlet temperature to 1570 K with efficiency increase to 47%. N₂O is eliminated at the elevated temperature in the Topping Combustor. Enabling technologies are: Hot Gas Cleanup and Topping Combustor. Demonstration is expected by 2010.
 - Integrated Gasification Combined Cycle is the cleanest of advanced coal fired technologies. The demonstration plants in the US were designed with relatively low cycle efficiency (~40%) but IGCC is capable of higher efficiencies through the application of advanced gas turbine technology and better subsystem integration. The disadvantage of presently higher installation cost compared to PC fired plant could be compensated for in the future by lower cost of mercury removal and more favorable conditions for CO₂ capture.
 - Interest in gasification has risen also because of favorable prospects for achieving in the near future a “zero emission” and near 60% efficient cycle by combinations of hydrogen production in coal gasification and use of fuel cell and gas turbine technology (Vision21).
 - While the cost of high efficiency power generation is expected to be reduced with time, it will likely to remain higher than that of a conventional plant mainly because of the low price of the saved coal. The real value of efficiency is environmental. In order to achieve diversity of fuel supply consistent with environmental quality, application of advanced coal based power generating technology would need to receive governmental financial incentive.
11. Roberts, A.G, K.K. Pillai and J.J. Stantan, Pressurized Fluidized Combustion in Fluidized Beds (J.R. Howard Ed.) Applied Science Publishers London (1983).
 12. Chan, L.K., A.F. Sarofim, J.M. Beér, Comb. Flame 52, pp.37-45 (1983).
 13. Beér, J.M. and R.V. Garland, Coal Fueled Combustion Turbine Cogeneration System with Topping Combustion, Trans. ASME J. of Engnr. for Gas Turbines and Power Vol. 119, no1, pp. 84-92 (1997).
 14. Pruschek, R., Goettlicher, G., Oeljeklaus, G., Haupt, G., Zimmermann, G., Power-Gen Europe 98 Milan, June 1998.
 15. Ruth L.A., US DOE Vision 21 Workshop FETC Pittsburgh, Pa., Dec 1998.
 16. Delot, P., DiMaggio, I., Jaquet, L., Roulet V., EDF Comparative Study of Clean Coal Technologies, Electricite de France Thermal Dept. (1996).
 17. Haupt, G. and Karg, J., Proc. of the 12th Conf. on the Electric Supply Industry (CEPSI) Pattaya/Thailand Nov. 1998.
 18. Herzog, H.J. and E.M. Drake, IEA/93/0E6, IEA Greenhouse Gas R&D Program, Cheltenham, UK (1993).
 19. Thambimuthu, K.V. and E. Croiset, Proc. Advanced Coal Based Power and Environmental Systems '98 Conference USDOE Morgantown. Paper 4.4. July 1998.

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References

1. Annual Energy Outlook 2001 Energy Information Administration, Office of Integrated Analysis and Forecasting U.S. Department of Energy, Washington, DC.
2. Skinner, D.G., The Fluidized Combustion of Coal, Review of the Findings of Research up to the beginning of 1969 National Coal Board R&D Department, London, UK, January 1970.
3. Beér, J.M., H.C. Hottel Plenary Lecture, 22nd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., pp.1-16 (1988).
4. Bowman, C.T., Progr. in Energy and Combustion Sci. p. 35, Pergamon Press (1975).
5. Couch, G.R., OECD Coal Fired Power Generation IEAPER/33 (1997).
6. Wendt, J.O., C.V. Sternling, M.A. Mafovich, 14th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., pp. 897-904 (1973).
7. Borio, R., Lewis, R., Keough, M.B., Booth R.C., Hall, R.E., Lott, R.A., Kokkinos, A., Gyorke, D.F., Durrant, S., Johnson, H.J., Kienkle, J.J., Proceedings of the 1991 Joint Symposium on Stationary Combustion NOx Control, EPRI, Palo Alto, Ca., USA., Rep. TR103265-V2 ,pp.49-68.
8. Folsom, B., Hong, C., Sommer, T., Pratapas, J.M., in the Proceedings of the 1993 Joint Symposium on Stationary Combustion NOx Control, EPRI, Palo Alto, Ca., USA, Rep. TR103265-V2 pp. 7A , 15-34.
9. Hauser, U., OECD/IEA Paris France pp 381-395 (1993).
10. Schilling, H.D., VGB Kraftwerkstechnik (73) 8., pp.564-576 (1993).

The Fischer-Tropsch process to clean fuels and chemicals.

Mark E. Dry
University of Cape Town.

For close on fifty years Sasol has been producing a variety of fuels and chemicals from synthesis gas produced by coal gasification. Two types of Fischer-Tropsch (FT) operations are used to convert the synthesis gas to the desired products, namely, the low temperature (LTFT) and the high temperature (HTFT) process.

The LTFT process is carried out in either multitubular, or preferably, in slurry bed reactors. The catalyst used can be either cobalt or iron based. At similar conditions cobalt based catalysts are capable of higher conversions. The main product is high value linear paraffin wax, which is used in a variety of applications. Alternatively the wax can be hydrocracked under mild conditions to produce a high yield of high quality diesel which combined with the straight-run FT diesel yields a fuel virtually free of aromatic and ring compounds and having a cetane number of about 70.

The HTFT process is carried out in fluidised bed reactors. The straight-run gasoline contains less than one percent benzene, the total aromatic content being only about 5%. The olefin content is about 70%. In order to increase the octane rating to the required level the naphtha is hydrotreated, the C_7^+ cut is reformed and the C_5/C_6 cut can be hydroisomerised. Extracting the highly valuable linear olefins as such or by converting them to valuable linear alcohols and then removing these naturally increases the octane rating of the remaining naphtha and hence less severe upgrading is required to meet the octane number specification.

Fischer-Tropsch Catalysts Supported on Sol-Gel Derived Silica

Brian C. Dunn, Paul Cole, Daniel J. Covington, Emily C. Heider,
Jennifer Gasser, Edward M. Eyring, Henk L. C. Meuzelaar, and
Ronald J. Pugmire

Departments of Chemistry and Chemical and Fuels Engineering
University of Utah
Salt Lake City, UT 84112

Introduction

Fischer-Tropsch synthesis has traditionally employed heterogeneous catalysts supported on metal oxides such as alumina, silica, or titania.¹ The metallic catalyst is typically loaded onto the support using either an impregnation or coprecipitation technique. Neither of these methods allows for strict control over the support properties which can play a crucial role in the Fischer-Tropsch synthesis.² Employing the sol-gel method to prepare amorphous silica from the polycondensation and hydrolysis of a suitable precursor, such as tetramethoxysilane, allows for control and manipulation of bulk support properties such as density, strength, pore diameter, and pore volume.³ The properties of the silica are determined by molar ratio of reactants, time required for gelation, aging period, drying technique, and drying time. Silica prepared by the sol-gel route can range from relatively dense, microporous xerogel to non-dense, mesoporous aerogel and can be controlled at all points in this continuum.

Heterogeneous catalysts prepared using sol-gel derived supports include platinum,⁴ iron,⁵ silver,⁶ gold,⁷ cobalt,⁸ and palladium.⁹ Fischer-Tropsch synthesis is typically performed utilizing either a cobalt or iron-based catalyst and the support properties greatly influence the product distribution by influencing heat and mass transport near the active metal catalyst particles. Sol-gel derived silica provides a unique opportunity for controlling the support properties and thus influencing the product distribution.

Experimental

Catalyst Preparation. The catalysts employed for Fischer-Tropsch synthesis were prepared by the sol-gel method. Water, methanol, and tetramethoxysilane (TMOS) were combined in a 16:4:1 molar ratio. An appropriate metal salt ($\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2$, RuCl_2) was dissolved in the water to yield 5-30% by weight of the final material. The mixture was sealed in glass vials and allowed to gel and age for 14 days. The xerogels were obtained by allowing the methanol and water to evaporate under ambient conditions over a period of 14 days. The xerogels were then crushed, reduced by heating in a stream of hydrogen, and sieved for size.

Fischer-Tropsch Synthesis. The reaction between H_2 and CO was carried out in a continuous flow reactor, 6 inches by 0.25 inch in diameter. Approximately 2 g of catalyst was used for each trial and discarded after the experiment. The flow of the reactants and carrier gas were maintained with appropriate mass-flow controllers (MKS Model 1179A) and the entire reactor system, including the transfer line, was heated to ensure that no condensation of the reaction products occurred. Routine measurement of reaction products was performed with online GC monitoring and reaction product identification was performed by condensing into cold *n*-octane, and analyzing by off-line GC/MS.

Results and Discussion

Catalyst Characterization. One of the catalysts was examined to determine some of the porosity properties of the sol-gel derived silica and the nature of the active metal catalyst, cobalt. **Table 1** lists

the specific surface areas of three different xerogel catalysts: unreduced $\text{Co}(\text{NO}_3)_2$, metallic cobalt, and a mixture of metallic cobalt and iron.

Table 1. BET Surface Areas

Catalyst	Surface Area (m^2/g)
$\text{Co}(\text{NO}_3)_2$	134
Co^0	338
Co^0/Fe^0	245

As can be seen from **Table 1**, the xerogel-based catalysts possessed a significant amount of surface area. The apparent increase in surface area upon reduction of the catalyst is most likely caused by expulsion of water and methanol, produced in the sol-gel reaction, from the pores of the catalyst when the catalyst was heated in a stream of hydrogen.

During reduction with hydrogen, the catalyst noticeably changed color from red (hydrated $\text{Co}(\text{NO}_3)_2$) to black and became ferromagnetic. This visual indication of reduction was confirmed by XRD analysis which indicated the presence of metallic cobalt and cobalt oxide. The XRD analysis also showed that the cobalt particles were about 6 nm in diameter.

Fischer-Tropsch Synthesis. Four different catalysts were employed to convert a mixture of hydrogen and carbon monoxide into higher hydrocarbons. Initial experiments were conducted using the cobalt xerogel and condensing the reaction products in cold *n*-octane. **Figure 1** shows an offline GC/MS chromatogram of the product mixture. Hydrocarbons lower than C_9 were not observable due to their volatility and the presence of the octane. The apparent product distribution is centered around C_{15} and the heaviest hydrocarbon observed was C_{32} . Each hydrocarbon consisted primarily of the *n*-alkane, but significant amounts of single unsaturated hydrocarbons were seen for the lower hydrocarbons ($\text{C}_9 - \text{C}_{15}$).

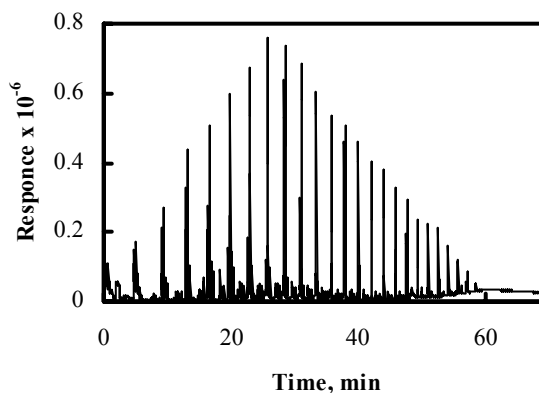


Figure 1. GC/MS chromatogram of Fischer-Tropsch product using 25% by weight cobalt xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Routine experiments were performed with online GC/FID detection of reaction products. **Figure 2** shows a chromatogram of the reaction products using an identical catalyst as that used in **Figure 1**. The lowest hydrocarbons, C_1 through C_4 , are not well resolved with C_5 appearing at about 7 minutes. The heaviest hydrocarbon observed with online monitoring was C_{18} rather than C_{32} as seen previously. Either the heavy products were not present in

high enough concentration for detection or the products were condensing somewhere in the reactor system prior to GC analysis.

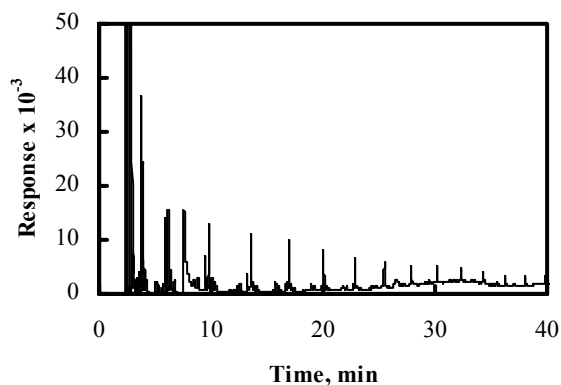


Figure 2. Online chromatogram of Fischer-Tropsch product using 25% by weight cobalt xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

A mixed cobalt/iron catalyst was used in the reactor and the product distribution is shown in **Figure 3**. The lower hydrocarbons can be seen prior to five minutes and appear to be somewhat resolved. Only a trace of heavy hydrocarbons was produced using this catalyst. Overall, the mixed cobalt/iron catalyst is much less active compared to the catalyst that contains only cobalt, although this may simply be caused by the different loadings of the cobalt.

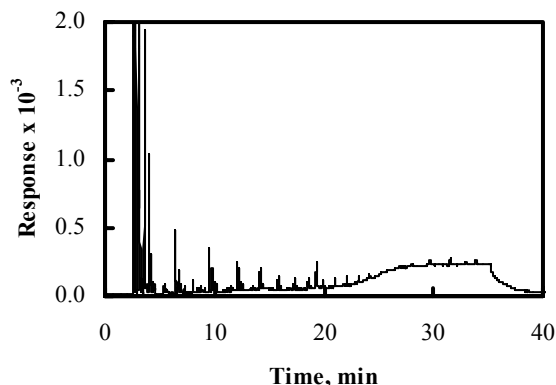


Figure 3. Online chromatogram of Fischer-Tropsch product using 15% by weight cobalt and 15% by weight iron xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Nickel and cobalt were combined during the sol-gel preparation of another catalyst and the Fischer-Tropsch product distribution appears in **Figure 4**. Very small amounts of hydrocarbon products were detected using this catalyst. However, the catalyst appears to be more selective for the heaviest hydrocarbons compared with either the cobalt only or cobalt / iron catalyst.

All of the catalysts have high selectivity towards the lower hydrocarbons, C₁ through C₄, which is undesirable. It should be possible to alter the reaction conditions (temperature, pressure, reactant flow rate, residence time) to decrease the selectivity for the lower hydrocarbons and increase the selectivity for higher hydrocarbons. It is possible that these sol-gel silica supported catalysts may be more sensitive to reaction conditions than

traditional catalysts. The cobalt likely resides in pores of the amorphous silica rather than simply on the outside surface of the support. This should provide for mass and heat transfer properties which are different than traditional catalysts.

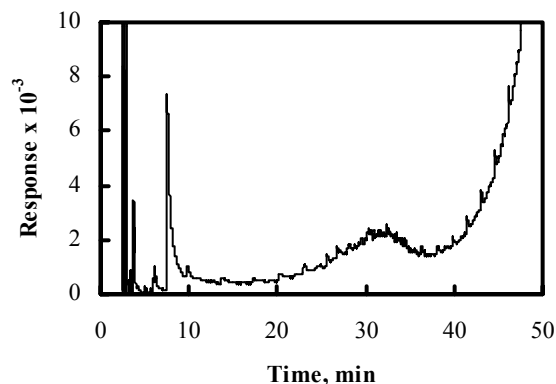


Figure 4. Online chromatogram of Fischer-Tropsch product using 15% by weight cobalt and 15% by weight nickel xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Additional experiments are currently underway to more fully characterize the support properties and to prepare a series of catalysts with a range of pore sizes and volumes to determine their effects on the Fischer-Tropsch synthesis.

Conclusions

The sol-gel technique for preparing amorphous silica is capable of incorporating metal salts into the structure of the support and, after reduction, the catalysts are active for Fischer-Tropsch synthesis. The unique nature of the sol-gel chemistry should allow for strict control and manipulation of the support properties in order to tune the catalyst for a desired product distribution.

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References

- (1) Jacobs, G.; Das, T. K.; Zhang, Y.; Li, J.; Racoillet, G.; Davis, B. H. *Appl. Cat. A* **2002**, 233, 263-281.
- (2) Li, S.; Krishnamoorthy, S.; Li, A.; Meitzner, G. D.; Iglesia, E. *J. of Catalysis* **2002**, 206, 202-217.
- (3) Bryans, T. R.; Brawner, V. L.; Quitevis, E. L. *J. Sol-Gel Sci. Tech.* **2000**, 17, 211-217.
- (4) Anderson, M. L.; Stroud, R. M.; Rolison, D. R. *Nano Letters* **2002**, 2, 235-240.
- (5) Leventis, N.; Elder, I. A.; Long, G. J.; Rolison, D. R. *Nano Letters* **2002**, 2, 63-67.
- (6) Morley, K. S.; Marr, P. C.; Webb, P. B.; Berry, A. R.; Allison, F. J.; Moldovan, G.; Brown, P. D.; Howdle, S. M. *J. Mater. Chem.* **2002**, 12, 1898-1905.
- (7) Pietron, J. J.; Stroud, R. M.; Rolison, D. R. *Nano Letters* **2002**, 2, 545-549.
- (8) Bae, D. S.; Kim, D. J.; Han, K. S.; Adair, J. H. *J. Ceram. Proc. Res.* **2002**, 3, 38-40.
- (9) Tanaka, S.; Mizukami, F.; Niwa, S.; Toba, M.; Maeda, K.; Shimada, H.; Kunimori, K. *Appl. Cat. A* **2002**, 229, 165-174.

SYNTHESIS OF MIXED ALCOHOLS OVER ADM CATALYSTS PROMOTED BY Ni AND Mn

Li Debao Qi Huijie Ma Yugang Li Wenhui
Sun Yuhua Zhong Bing

State Key Laboratory of Coal Conversion, Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, P.R. China 030001

Introduction: Many attentions have been paid on the developments of catalysts for mixed alcohol synthesis from syngas in recent years. Among the various catalysts, alkali-doped molybdenum sulfide (ADM) catalyst was considered as one of the most promising systems because of its high selectivity towards alcohols and high activity of water-gas shift reaction, in particular, resistance of S poisoning in the feed gas [1-4]. ADM catalyst modified by Ni and Mn was prepared and the performance for higher alcohols synthesis was investigated in this paper. It was found that the Ni element could promote the activity and selectivity to C_2^+OH , however the selectivity to hydrocarbons also increased. Mn-ADM catalyst showed different performance from Ni-ADM catalyst. Modified by Mn and Ni, the catalyst showed high selectivity to alcohols because of the inhibition of formation of hydrocarbons and the selectivity to C_2^+OH increased sharply. It implied that the structure of Ni played an important role for the performance of higher alcohols synthesis. The characterizations such as XRD, SEM, EPMA were carried out to illustrate the influence of the promoters on the performance of higher alcohols synthesis.

Experimental: The Ni (Mn)-ADM and Ni-Mn-ADM catalysts were prepared by co-precipitation from a solution of aqueous $(NH_4)_2MoS_4$, $Ni(C_2H_3O_2)_2$ and (or) $Mn(C_2H_3O_2)_2$ under pH=3-4. The precipitate was dried and mixed with a mount of K_2CO_3 and then decomposed in nitrogen. The compositions was as follows: Mo:K:Ni:Mn=1:0.7:0.33:0.03 (mole ratio). The reactions were carried out in a stainless fixed-bed reactor. The reaction condition was: 10.0MPa, GHSV=5000h⁻¹, 300 °C, $H_2/CO=2.0$. The products were analyzed by gas chromatographs. The data were taken at steady-state after 100hr on-stream. X-ray powder diffraction (XRD) patterns of the tested catalysts were obtained using a Rigaku D/Max 2500 powder diffractometer using Cu K α radiation as the X-ray source. SEM images and X-ray maps were obtained using a LEO 438VP SEM (20KV) and a KEVEX energy dispersive X-ray spectroscopy (probe current 1.5nA).

Results and Discussion:

The results of carbon monoxide hydrogenation were listed in Table1 and Table2. It can be seen that for Ni-ADM catalyst, the CO conversion and the selectivity of both higher alcohols and hydrocarbons increased compared with that of ADM catalyst. The remarkable effect of Ni promoter might be ascribed to the intrinsically nature that nickel is activity element for carbon monoxide hydrogenation especially methanation. It was apparently that Ni was bi-functional, the first is the promotion effect for chain propagation for higher alcohols, and the second is the higher activity for synthesis of hydrocarbons, especially CH_4 . The dual effects of Ni promoter implied that it could offer different activity sites for higher alcohols and hydrocarbon simultaneously. Recent investigation on nickel catalyst showed that Ni containing catalyst had excellent ability for CO insertion, which was extremely important significance for higher alcohol synthesis [5]. Studies of metal catalysts for syngas reaction with varying dispersion revealed that the structure of some active element (such as Ni, Pd) played an important role for the reaction of CO hydrogenation: catalysts with small crystallites produce alcohol while larger crystallites produce methane [6-7]. As a

result, the increasing of CO conversion and selectivity of alcohols especially C_2^+OH over Mn-Ni-ADM catalyst might suggested that the promoter Mn had strong influence on the distributions and morphology of Ni that were closely related to the active sites for synthesis alcohols.

The XRD patterns (Fig.1) showed that ADM-based catalysts all had phase of poorly crystalline hexagonal MoS_2 , the values of 2θ were 14.4, 33.5, 39.5 and 58.4. The pattern of Ni-ADM showed strong crystal phases of NiS_x , the 2θ were 26.1, 29.8, 30.8 and 53.6, however for Mn-Ni-ADM catalyst, such diffraction peaks as that of NiS_x disappeared clearly. Fig.2 showed the SEM images and element maps of Ni of Ni-ADM and Mn-Ni-ADM catalysts. The X-ray maps showed that lateral distributions of Mo, S, K had little difference of the two catalysts, however the distribution of Ni was changed greatly due to the addition of Mn. It was clear that for Ni-containing ADM catalysts, the structure and the dispersion of Ni on the catalyst surface had great influence on performance of synthesis alcohols. The promoter Mn inhibited forming of larger crystal of NiS_x and improved the dispersion of Ni species due to the interaction between Ni and Mn. The strong synergy effect of Ni and Mn could offer more active sites for synthesis alcohols.

Table1 Performance of CO hydrogenation over ADM catalysts

Catalyst	CO conv. (mol%)	STY (g/(ml · h))		Selectivity (mol%-freeCO ₂)	
		ROH	C2+OH	Alcohols	Hydrocarbons
ADM	11.4	0.321	0.091	68.27	31.73
Ni-ADM	28.8	0.465	0.181	53.5	46.5
Mn-ADM	10.5	0.37	0.092	75.49	24.51
Mn-Ni-ADM	24.3	0.39	0.206	76.19	23.81

Table2 Product distributions of CO hydrogenation

Catalyst	Hydrocarbons (mol.%)				Alcohols (wt%)				
	C1	C2	C3	C4+	C1	C2	C3	C4	C5+
ADM	74.01	20.20	4.71	1.09	70.64	19.77	7.40	2.02	0.16
Ni-ADM	93.32	4.75	1.92	/	70.10	25.10	3.94	0.81	0.05
Mn-ADM	76.80	19.81	2.98	0.41	77.02	17.01	3.84	1.68	0.45
Mn-Ni-ADM	81.00	15.79	2.71	0.51	41.97	36.88	14.93	5.03	1.20

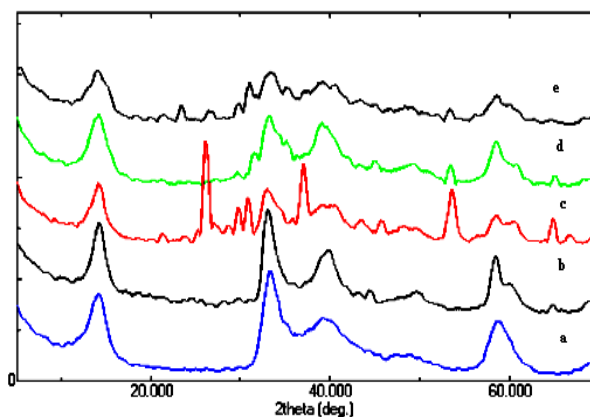
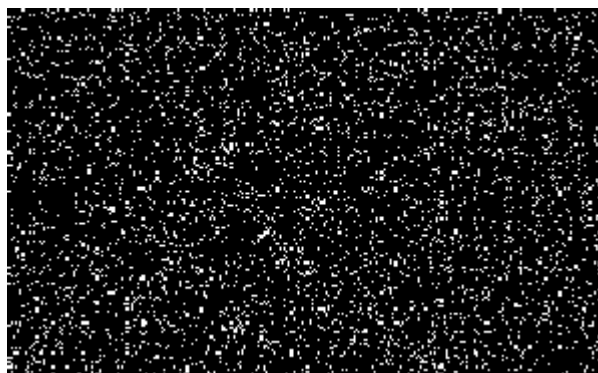


Fig.1. The X-Ray Diffraction Patterns of Molybdenum Sulfides-based catalysts
a. MoS_2 ; b. ADM; c. Ni-ADM; d. Mn-ADM; e. Mn-Ni-ADM



(a) Ni-ADM



(b) Mn-Ni-ADM

Fig.2. Electron probe analysis of Ni-ADM and Mn-Ni-ADM catalysts (1000 \times) X-ray map of Ni

References:

1. Xu X.D., et al., Catal. Today. 2(1987)125.
2. Zhenyu Liu, Xianguo Li, et al., Ind.Eng.Chem.Res. 36(1997)3085.
3. Murchison, C.B., Conway, M.M., Stevens, R.R. and Quarder, G.J., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M.J. Phillips and M. Ternan, Eds.), Vol.2, p.626. Chem. Institute of Canada, Ottawa, 1988.
4. Santiesteban, J.G., Bogdan, C.E., Herman, R.G., and Klier, K., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M.J. Phillips and M. Ternan, Eds.), Vol.2, p.561. Chem. Institute of Canada, Ottawa, 1988.
5. Steven S.C. CHUANG and Shyh-Ing PIEN, Catal. Lett. 3(1989)323.
6. Zhongrui Li, Yilu Fu et al., Catal. Lett. 65(1989)43.
7. V. Ponc, Catal. Today. 12(1992)227.

THE ROLE OF IRON PROMOTER IN HIGHER ALCOHOLS SYNTHESIS: EFFECT OF PREPARATION PARAMETER ON THE Cu/Mn/Fe/ZrO₂ CATALYST

Xu Run, Ma Zhongyi, Yang Cheng, Wei Wei, Sun Yuhan

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, TaiYuan, China, 030001

Introduction

The elucidation of the effect of the preparation on the nature and structure of a catalyst is of considerable importance for catalyst design. In previous work [1], Cu/ZrO₂ catalysts prepared by different method were tested by carbon monoxide hydrogenation and characterized by means of various surface and structure. And it was found that a proportion for higher alcohols was reached over iron, cobalt and nickel modified Cu/ZrO₂ catalysts [2]. Among them, iron modified Cu/Mn/ZrO₂ catalysts showed good performance in higher alcohol synthesis. The role of iron has been described promoted carbon chain growth in the literature. Therefore, the effect of iron on the catalysts was investigated by different prepared method.

Results and Discussion

Carbon monoxide hydrogenation was investigated on Fe-modified Cu/Mn/ZrO₂ catalysts. The catalysts were prepared by wetness impregnation method (CMZF-i) and co-precipitation (CMZF-c) method. When Fe was added as a promoter, CO hydrogenation products over the catalyst exhibited an obvious change from methanol to C₂₊OH. The alcohol yield of 0.26g/(mL•h) with a C₂₊OH selectivity of about 22% was obtained over CMZF-i catalyst under the moderate reaction condition (573K, 6.0MPa, 3000h⁻¹). The activity and selectivity of CMZF-i catalyst was obviously higher than CMZF-c. The curves of CO conversion – higher alcohol selectivity was showed in Fig.1 and 2. It was found that the methanol selectivity decreased and the iso-butanol selectivity increased sharply regular with the CO conversion raise up in CMZF-c catalyst (Fig 1). However, it was not that in CMZF-i catalyst. The linear alcohol selectivity increased synchronously expect methanol. The experimental results indicated that there have different mechanisms of alcohols synthesis on catalysts in CO hydrogenation [3]. So the effect of iron was different. The catalysts have been characterized by the TEM (Fig. 3). It was found the CMZF-i catalyst could get smaller particles than the CMZ sample; the particle size distribution of the CMZF-i catalyst was in 80-120 nm. And the particle of CMZF-c was same as the CMZ catalyst with an average particle size of 180-220 nm. So the iron in CMZF-i catalyst could increase the dispersal of catalyst. Fig. 4 illustrates TPR curves for the copper catalyst with different prepared method. Only one peak was seen during the reduce process. This peak was considered to the reduction of CuO to Cu [4]. The curve of CMZF-c was similar to the CMZ. But the peak shifted to higher temperature in the CMZF-i catalyst. The reduction of CuO in catalysts became harder. The results indicate that Fe loaded by an impregnation method could improve the dispersal of catalysts. On the other hand, the strong interaction occurred because of highly dispersed Cu, Fe or Mn. So the reduction of CuO in catalysts became harder. It is suggested that the effect of iron in catalysts was not only promoted carbon chain growth but also modified the structure of catalysts.

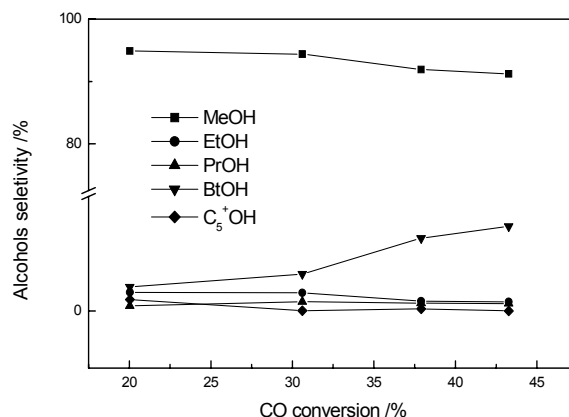


Fig 1 The performance of CMZF-c catalyst in higher alcohol synthesis

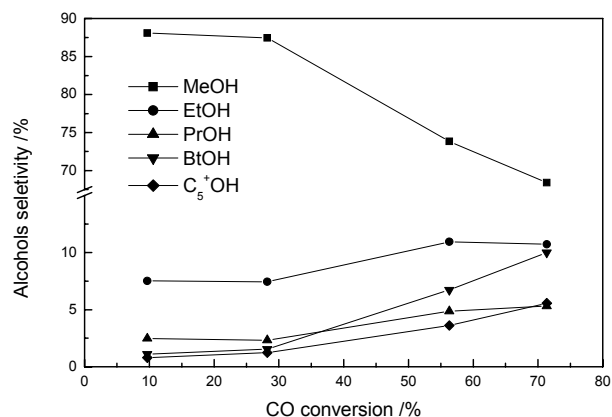


Fig 2 The performance of CMZF-i catalyst in higher alcohol synthesis

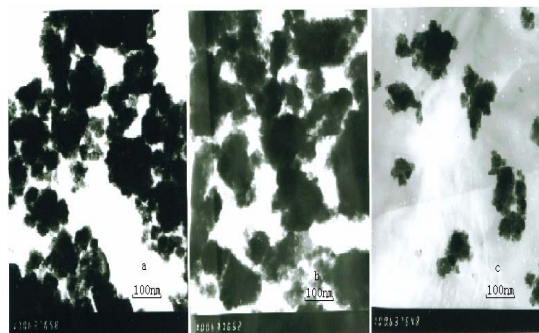


Fig 3 The TEM photo of catalysts a: CMZ, b: CMZF-c, c: CMZF-i

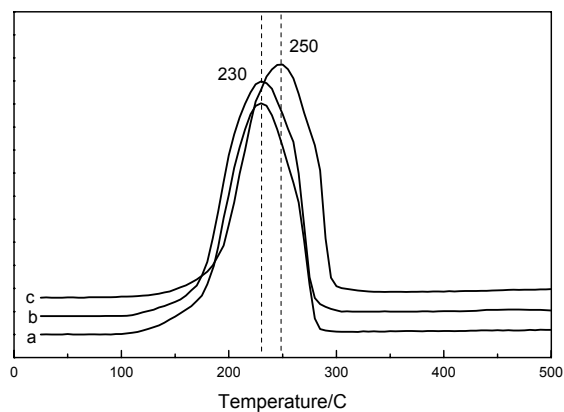


Fig 4 The H₂-TPR curve of catalysts
a: CMZ, b: CMZF-c, c: CMZF-I

References

- (1) Yuhua Sun and P.A.Sermon, *J.C.S.Chem.Comm.*, 1 (1993) 242
- (2) Ning Zhao, Run Xu, Wei Wei and Yuhua Sun, *React. Kinet. Catal. Lett.*, 75 (2002) 297
- (3) Xiaoding Xu, E. B. M.Doesburg, J. J. F. Scholten, *Catal. Today*, 2 (1987) 125
- (4) M. Shimokawabe, H. Asakawa, N. Takezawa, *Appl. Catal.*, 59 (1990) 45